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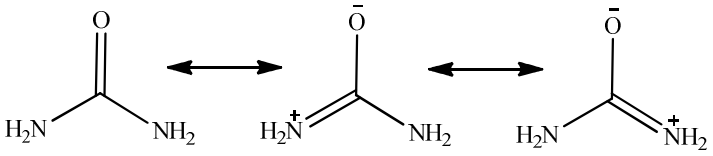
Synthesis methods of phosphorylated carbamide containing acyclic and heterocyclic compounds

In the paper, for the first time, an attempt of systematization of knowledge in the field of reactions of ureas and their heterocyclic derivatives with phosphorus containing reagents has been carried out. In the review due to the significant differences in the substrates and reagents used, methods for producing phosphorylated nitrogen-containing compounds according to their final structure are grouped in three directions of their formation — the synthesis of acyclic, monocyclic and bicyclic ureas. Thus, the methods for the production of acyclic N-phosphorylated ureas by reactions of the corresponding N-phosphoisocyanates with aliphatic and aromatic amines of various structures are considered, and rarely used alternative methods for the synthesis of such compounds are considered. An analysis of the known methods for the synthesis of phosphorylated monocyclic carbamide-containing compounds suggests that: five-membered phosphazacycles, most of them are represented by imidazolidine structures, while tetracyclic phosphazacycles are diazaphosphetidinones, and six-membered phosphazacycles are diazophosphorins and triazaphophorphoryphorphoridine. The synthesized and studied phosphorylated bicyclic bisurea are represented by diphosphadione, diphosphaspirooctanedione, and phosphorylated tetraazabicyclo octionic structures. It was concluded that, on the basis of the systematization of the results of experimental studies on the methods of synthesis of phosphorylated ureas, it can be expected that their development will allow finding ways to obtain new highly effective drugs and synthons of their production.

Keywords: urea, phosphorylation, heterocyclic compounds, N-phosphoisocyanates, imidazolidines, diazaphosphetidinones, diazophosphorins, triazaphosphorinandionones, diphosphadiones, diphosphaspiroctanediones, phosphorylated tetraazibicyclooctandiones, glycoluryl.

Introduction

The chemistry of acyclic and cyclic ureas, primarily due to the availability and polyfunctionality of the latter, has undergone rapid development in various spheres of human activity. Since F. Wöhler discovered the synthesis of urea 1 based on inorganic substances, urea has always been the object of close research attention of both chemists and pharmacological specialists.



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More than one and a half-century history of urea chemistry was marked by the creation on their basis of many dozens of valuable substances that have been used as effective drugs [1], herbicides [2], fertilizers [3] and other biologically active compounds.

Despite the wide popularity of ureas as objects of the synthetic "simulator", the chemistry of ureas is constantly evolving, and the traditional ways of their use in organic synthesis are constantly being improved.

Synthesis and study of phosphorus-containing compounds based on urea is one of the progressive trends in the development of urea chemistry. The combination of urea fragments and phosphoryl groups in a molecule makes it possible to impart specific useful properties to the target substance, which is the subject of a wide discussion of methods for producing phosphorylated ureas [4, 5].

Some of the acyclic organophosphorus nitrogen-containing compounds are being used as therapeutic drugs, such as zoledronic acid (zoledronate), which has a selective effect on bone tissue and is therefore used in the treatment of osteoporosis [6]. One of the widely used non-selective systemic herbicides is glyphosate (N-(phosphonomethyl)-glycine) [7]. Due to its unique properties, this drug is the first in the world production of herbicides. In addition, glyphosate is used in the production of polymeric materials, especially non-combustible and chemically resistant ion exchange resins, used in the analysis and production of highly pure substances, and other areas of technology.

Monocyclic nitrogen-containing heterocycles containing a urea moiety in the cyclic skeleton are attractive because the latter is often a key multifunctional structural element of these compounds. The presence of N- and O-nucleophilic reaction centers in the urea molecule promotes their cyclization under the action of various phosphorylating agents [8].

Generally the nature and direction of cyclization is influenced, first of all, by the nature of the substituent at the amide nitrogen atom of urea and the conditions of the reaction studied. The direction of the reactions of phosphazacyclization of urea by ethers of chlorine derivatives of phosphoric acids often depends on the coordination number of phosphorus.

The development and improvement of known methods for the synthesis and functionalization of monocyclic nitrogen-containing heterocycles is greatly stimulated by their well-known participation in human activity. For example, among cyclic compounds, based on phosphorylated ureas, polymeric compounds [9] and drugs with high pesticidal, anticholinesterase, antiviral, and antimicrobial activity [10] are found.

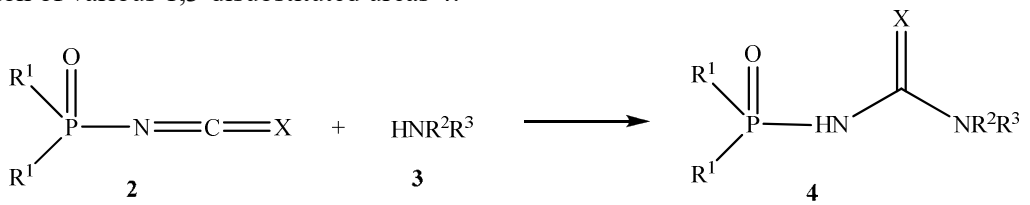
The chemistry of bicyclic bisureas occupies a special place among nitrogen-containing heterocyclic compounds, primarily due to the framework structure and the presence of multifunctional reaction centers. 2,6-diacetyl glycoluryl diphosphonic acid is known among the phosphorylated bicycles, which has been used as an electrode modifier for quantitative determination of cholesterol by voltammetry [11].

Since there is currently no information in the available literature, summarizing synthesis and research methods of chemical properties of phosphorylated urea-containing acyclic and heterocyclic compounds, we have systematized knowledge in this area, which was the basis for writing an independent review article. The review of literature data is systematized according to the methods of synthesis of phosphorylated acyclic, monocyclic and bicyclic carbamide containing compounds.

1 Synthesis methods of phosphorylated acyclic ureas

1.1 Isocyanate method for producing acyclic N-phosphorylated ureas

Among the relatively large number of methods for producing N-phosphorylated ureas, reactions based on the interaction of the corresponding N-phosphoisocyanates with various amines are prevalent. Methods for obtaining phosphorus-containing isocyanates and their chemical properties are discussed in the review [12], where the reactions of the latter with various organic substrates, including amines, are also given. Thus, according to the general scheme 1, the reaction of isocyanates 2 with primary and secondary amines 3 leads to the formation of various 1,3-disubstituted ureas 4:



Scheme 1

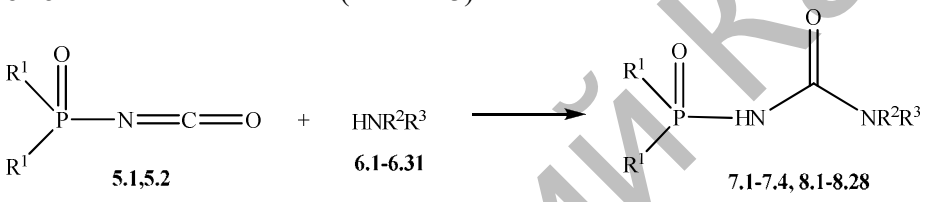
This method is widely used, including for the synthesis of various ureidophosphoric acids [13–21].

It was shown [13] that fluorinated 5.1 phosphoisocyanates in reactions with primary and secondary amines 6.1–6.4 turned out to be convenient reagents for the synthesis of fluorine derivatives of N-alkyl- and N-aryl-substituted phosphorylated urea 7.1–7.4 (Scheme 2).

One of the variants of the synthesis of arylcarbamidophosphoric acids is [14] that isocyanate phosphoric acid chloride **5.2** can easily react with various amines 6.4–6.21. However, the authors emphasize that aromatic amines with electron-withdrawing substituents (such as p-chloro 6.10 and p-bromoaniline 6.11, o- and m-nitroaniline 6.5 and 6.6, etc.) react slower. Even greater difficulties are caused by interactions with secondary arylamines (diphenylamine 6.21), but at the same time, the product yield of 8.1–8.18 are 62–99 % (Scheme 2).

The authors of [15], developing their work [16, 17] aimed at crystal structure, biological activitystudy and some electronic aspects, synthesized the already known series of dichlorophosphoryl derivatives of N-substituted phenylureas 8.1–8.6 and supplemented it with similar interactions of dichlorophosphoisocyanate 5.2 with the corresponding aryl amines 6.22–6.26 with the formation of compounds 8.19–8.23 (Scheme 2). Based on the compounds obtained 8.1–8.6, 8.19–8.23, the authors synthesized a number of biologically active diazaphosphorinanes 45.1–45.11 and diazaphospholanes 46.1–46.11 for further study (Scheme 12).

In order to search for new biologically active compounds, the authors of [18–20] using known methods [14, 21] synthesized a similar series of dichlorophosphoryl derivatives of N-substituted phenylureas 8.7–8.10, 8.24–8.28 using the corresponding amines 6.10–6.13, 6.27–6.31 (Scheme 2) for further condensation of ureas 8.7–8.10, 8.24–8.28 with various substrates (Scheme 3).



5. 1: R^1 = F
2: R^1 = Cl

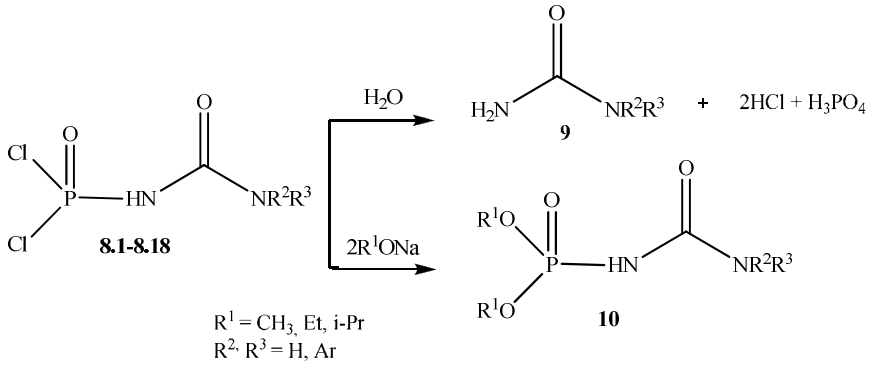
7. 1: R^1 = F, R^2 = H, R^3= Ph
2: R^1 = F, R^2 = H, R^3= C_2H_5
3: R^1 = F, R^2 = R^3= C_2H_5
4: R^1 = F, R^2 = $C_6H_5CH_3$, R^3 = CH_3

6. 1: R^2 = 4-CH_3-C_6H_4, R^3 = CH_3
2: R^2 = H, R^3 = C_2H_5
3: R^2 = R^3 = C_2H_5
4: R^2 = H, R^3 = Ph
5: R^2 = H, R_3 = 2-NO_2-C_6H_4
6: R^2 = H, R^3 = 3-NO_2-C_6H_4
7: R^2 = H, R^3 = 4-NO_2-C_6H_4
8: R^2 = H, R^3 = 2-CH_3-C_6H_4
9: R^2 = H, R^3 = 4-CH_3-C_6H_4
10: R^2 = H, R^3 = 4-Cl-C_6H_4
11: R_2 = H, R_3 = 4-Br-C_6H_4
12: R^2 = H, R^3 = 4-CH_3O-C_6H_4
13: R^2 = H, R^3 = α-$C_{10}H_7$
14: R^2 = H, R^3 = 4-C_2H_5-C_6H_4
15: R^2 = H, R^3 = 4-i-C_3H_7-C_6H_4
16: R^2 = H, R^3 = 4-C_2H_5O-C_6H_4
17: R^2 = H, R^3 = 2-NO_2-C_6H_4-4-CH_3
18: R^2 = H, R^3 = 2,4,6-Cl-C_6H_2
19: R^2 = H, R^3 = β-$C_{10}H_7$
20: R_2 = C_2H_5, R_3 = C_6H_5
21: R_2 = R_3 = Ph
22: R^2 = H, R^3 = 4-CN-C_6H_4
23: R_2 = H, R_3 = 4-F-C_6H_4
24: R_2 = H, R_3 = 3-F-C_6H_4
25: R_2 = H, R_3 = 2-F-C_6H_4
26: R^2 = H, R^3 = 3-CH_3-C_6H_4
27: R^2 = H, R^3 = 2,4-$(CH_3)_2$-C_6H_4
28: R^2 = H, R^3 = 3,4-$(CH_3O)_2$-C_6H_4
29: R^2 = H, R^3 = CH_2-C_6H_4-Cl-2
30: R^2 = H, R^3 = C_6H_{11}-c
31: R^2 = H, R^3 = C_2H_4O-c

8. 1: R^1 = Cl, R^2 = H, R^3 = Ph
2: R^1 = Cl, R^2 = H, R_3 = 2-NO_2-C_6H_4
3: R^1 = Cl, R^2 = H, R^3 = 3-NO_2-C_6H_4
4: R^1 = Cl, R^2 = H, R^3 = 4-NO_2-C_6H_4
5: R^1 = Cl, R^2 = H, R^3 = 2-CH_3-C_6H_4
6: R^1 = Cl, R^2 = H, R^3 = 4-CH_3-C_6H_4
7: R^1 = Cl, R^2 = H, R^3 = 4-Cl-C_6H_4
8: R^1 = Cl, R_2 = H, R_3 = 4-Br-C_6H_4
9: R^1 = Cl, R^2 = H, R^3 = 4-CH_3O-C_6H_4
10: R^1 = Cl, R^2 = H, R^3 = α-$C_{10}H_7$
11: R^1 = Cl, R^2 = H, R^3 = 4-C_2H_5-C_6H_4
12: R^1 = Cl, R^2 = H, R^3 = 4-i-C_3H_7-C_6H_4
13: R^1 = Cl, R^2 = H, R^3 = 4-C_2H_5O-C_6H_4
14: R^1 = Cl, R^2 = H, R^3 = 2-NO_2-C_6H_4-4-CH_3
15: R^1 = Cl, R^2 = H, R^3 = 2,4,6-Cl-C_6H_2
16: R^1 = Cl, R^2 = H, R^3 = β-$C_{10}H_7$
17: R^1 = Cl, R_2 = C_2H_5, R_3 = C_6H_5
18: R^1 = Cl, R_2 = R_3 = Ph
19: R^1 = Cl, R^2 = H, R^3 = 4-CN-C_6H_4
20: R^1 = Cl, R_2 = H, R_3 = 4-F-C_6H_4
21: R^1 = Cl, R_2 = H, R_3 = 3-F-C_6H_4
22: R^1 = Cl, R_2 = H, R_3 = 2-F-C_6H_4
23: R^1 = Cl, R^2 = H, R^3 = 3-CH_3-C_6H_4
24: R^1 = Cl, R^2 = H, R^3 = 2,4-$(CH_3)_2$-C_6H_4
25: R^1 = Cl, R^2 = H, R^3 = 3,4-$(CH_3O)_2$-C_6H_4
26: R^1 = Cl, R^2 = H, R^3 = CH_2-C_6H_4-Cl-2
27: R^1 = Cl, R^2 = H, R^3 = C_6H_{11}-c
28: R^1 = Cl, R^2 = H, R^3 = C_2H_4O-c

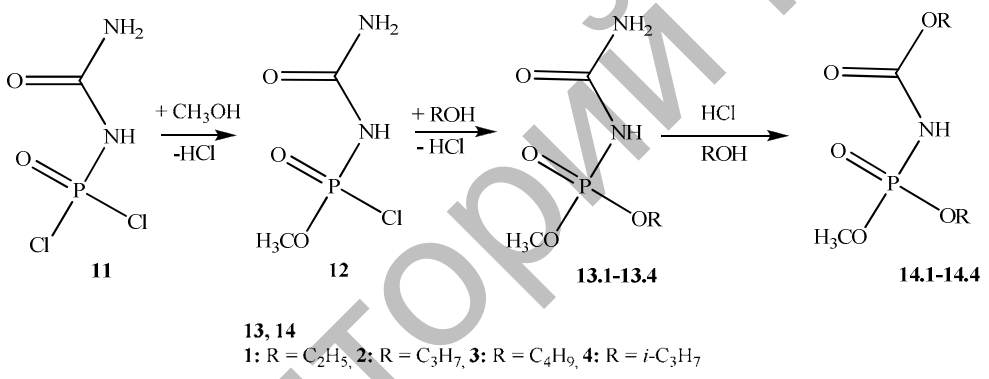
Scheme 2

Arylcarbamidophosphoric acid chlorides 8.1–8.28 [14] are crystalline compounds difficultly soluble in benzene, ether, carbon tetrachloride, chloroform, slowly decompose in air, slowly react with water at room temperature, but when heated, the hydrolysis passes quickly. Water is mainly attached through the P–N bond, since it was found that the main products of hydrolysis are N-aryl urea 9, while the acid chlorides 8.1–8.18 (Scheme 2) give the corresponding esters 10 [14] under the action of alcoholates (Scheme 3).



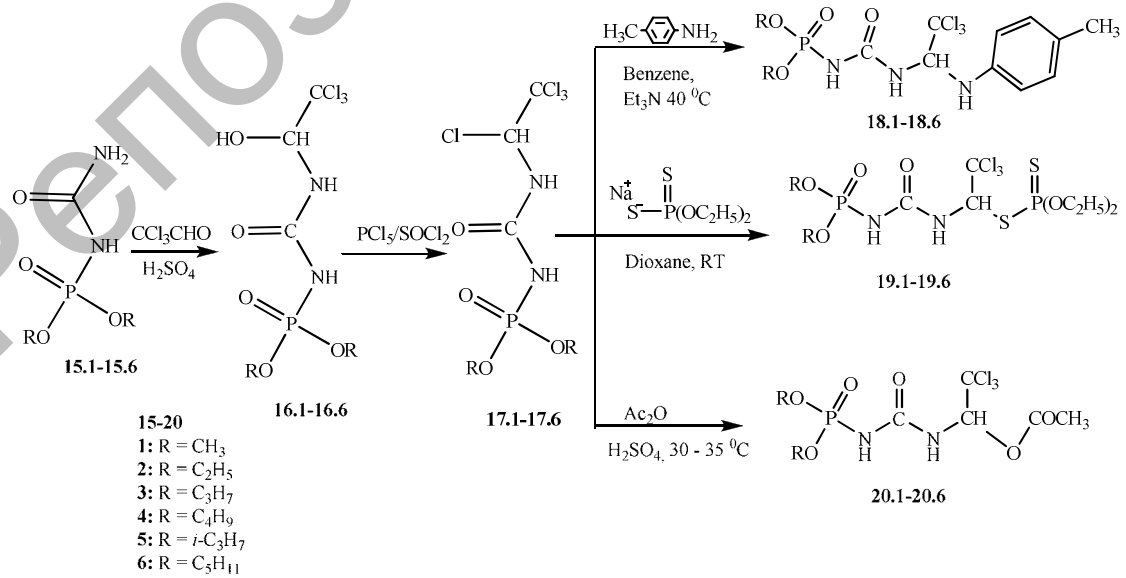
Scheme 3

In a number of subsequent works, this method of synthesis of phosphorylated ureas was further developed [22, 23]. Thus, it was shown [22] that the reaction of ureidophosphoric acid dichloride 11 with alcohols in the presence of hydrogen chloride proceeds in steps, which makes it possible to obtain dialkyl esters of ureidophosphoric acid 13.1–13.4 with different alkoxy substituents at phosphorus atoms. Under the action of methanol on 11, ureidophosphoric acid methyl ester chloride 12 was obtained, which was separated from the reaction mass and further treated with an excess of dry alcohols (ethanol, propanol, butanol, isopropanol) to obtain N-(methoxy alkoxyphosphoryl) ureides 13.1–13.4. When the esters 13.1–13.4 are heated in the presence of alcohol and an excess of HCl, dialkyl esters of urethanphosphonic acid 14.1–14.4 are formed (Scheme 4).



Scheme 4

To study the biologically active properties of organophosphorus compounds, N-alkylphosphoryl urea 15.1–15.6 was condensed with chloral (Scheme 5) [23].

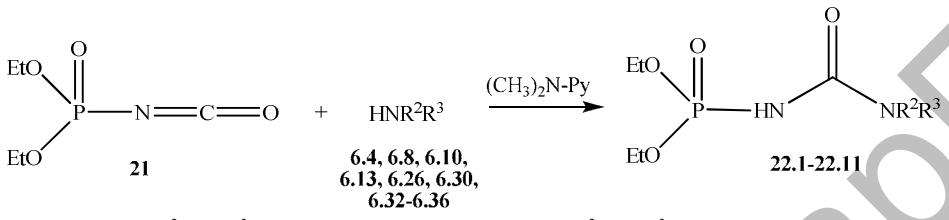


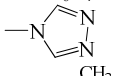
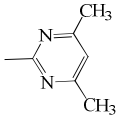
Scheme 5

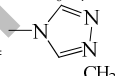
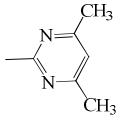
The hydroxyl group in the resulting products 16.1–16.6 is replaced by chlorine in reactions with chlorinating agents such as PCl_5, $SOCl_2$. In turn, the resulting N-dialkylphosphoryl-N'-1,2,2,2-tetrachloroureas 17.1–17.6 react with amines, alcohols, salts, forming the corresponding substituted urea 18–20 with yields of 43–95 % (Scheme 5).

For the substances 18–20 obtained, their antiviral activity was reported in [23].

Esters of ureidophosphoric acid 22.1–22.11 can be obtained according to a scheme similar to the reaction of isocyanates (Scheme 2). For example, in the work [24], phosphoryl isocyanate ethyl ether 21 reacted with aryl and hetarylamines 6.4, 6.8, 6.10, 6.13, 6.26, 6.30, 6.32–6.36 in the presence of catalytic amounts of 4-dimethylaminopyridine (Scheme 6).

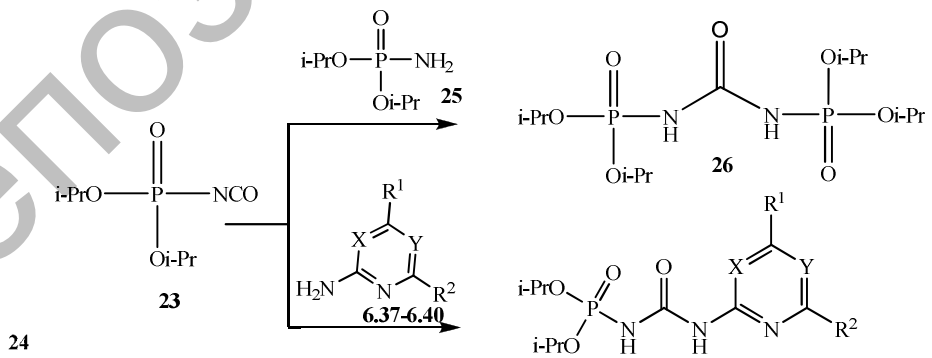


6
4: R^2 = H, R^3= Ph
8: R^2 = H, R^3= 2-CH_3-C_6H_4
10: R^2 = H, R^3= 4-Cl-C_6H_4
13: R^2 = H, R^3= α-$C_{10}H_7$
26: R^2 = H, R^3= 3-CH_3-C_6H_4
30: R^2 = H, R^3= C_6H_{11}-c
32: R^2 = H, R^3= $PhCH_2$
33: R^2 = H, R^3= 2-Cl-C_6H_4
34: R^2 = H, R^3= 3-Cl-C_6H_4
34: R^2 = H, R^3= 
36: R^2 = H, R^3= 

22
1: R^2 = H, R^3= Ph
2: R^2 = H, R^3= 2-CH_3-C_6H_4
3: R^2 = H, R^3= 4-Cl-C_6H_4
4: R^2 = H, R^3= α-$C_{10}H_7$
5: R^2 = H, R^3= 3-CH_3-C_6H_4
6: R^2 = H, R^3= C_6H_{11}-c
7: R^2 = H, R^3= $PhCH_2$
8: R^2 = H, R^3= 2-Cl-C_6H_4
9: R^2 = H, R^3= 3-Cl-C_6H_4
10: R^2 = H, R^3= 
11: R^2 = H, R^3= 

Scheme 6

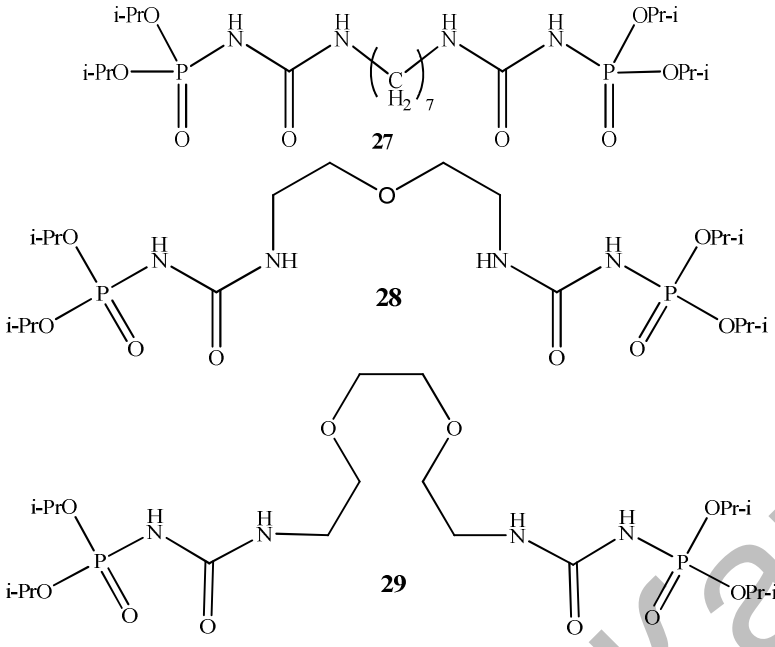
In order to search for biologically active compounds based on esters of substituted phosphorylated ureas, reactions [25] of diisopropoxyphosphoryl isocyanate 23 with some heterocyclic amines 6.37–6.40 in inert atmosphere with subsequent production of urea derivatives 24.1–24.4 were studied (Scheme 7). The authors also noticed that the interaction of diisopropoxyphosphoryl isocyanate 23 with diisopropoxyphosphorylamide 25 gives rise to diphosphorylated symmetric urea 26.



24
1: X=Y=N, R^1=R^2=NH_2
2: X=CH, Y=CH-CH_3, R^1= CH_3, R^2 = OCH_3
3: X=Y=CH, R^1= CH_3, R^2 = H
4: X=CH, Y=CH-CH_3, R^1=R^2=H

Scheme 7

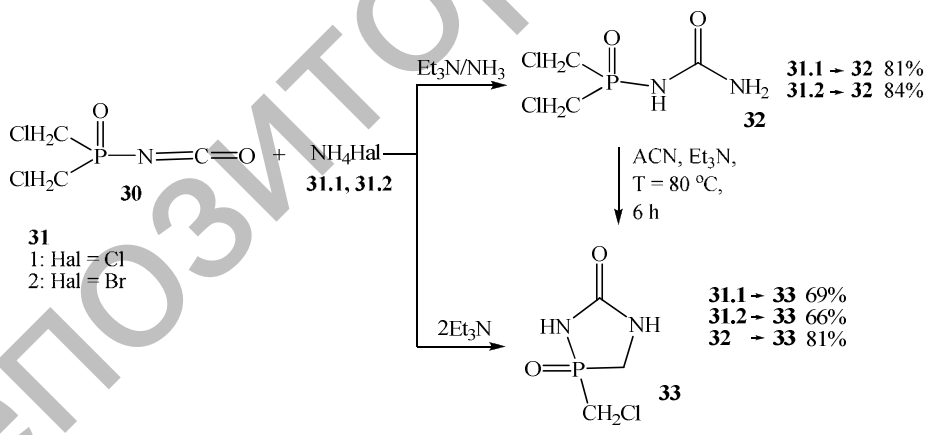
Similarly, N-phosphorylated bromides 27–29 based on reactions of diisopropoxyphosphoryl isocyanate 23 and α, ω-diamines were synthesized in order to study the extractive properties of Eu (III) [26] (Scheme 8).



Scheme 8

Studied podands 27–29 differ in the link between two phosphorylated urea fragments. Bonds with oxygen atoms can form a crown ether cavity, which can compete with the complexing ends of the bidentate parts of the extractant.

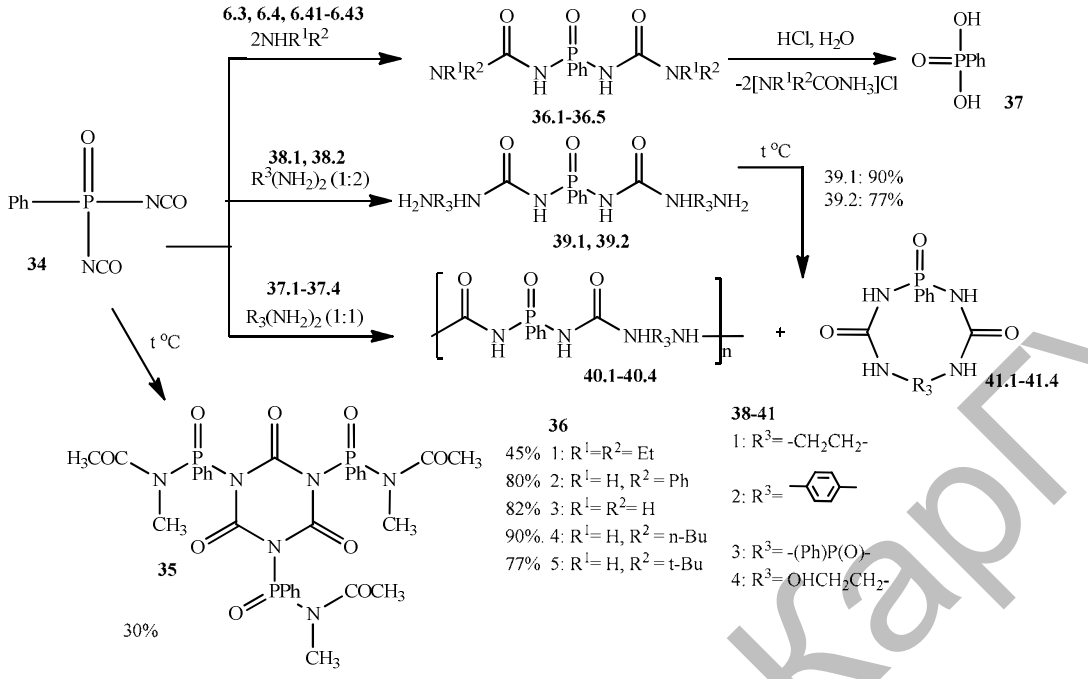
To obtain monosubstituted phosphorylureas, it is also possible to use both ammonia [27] and ammonium halides 31.1, 31.2 (Scheme 9). [28] showed that bis(chloromethyl)phosphine isocyanate 29 reacts with chloride 31.1 or ammonium bromide 31.2 at room temperature in chloroform and an equimolar amount of triethylamine, which leads to the formation of N-[bis(chloromethyl)phosphinoyl] urea 32 with outputs 81 and 84 %, respectively (Scheme 9):



Scheme 9

However, it was found that a double excess of triethylamine and boiling the reaction mass for 12 hours, lead to the formation of phosphazocyclic urea 33 with 69 % yield when using ammonium chloride 31.1 and 66 % when using ammonium bromide 31.2 Heating urea 32 in anhydrous acetonitrile with an equimolar amount of triethylamine during 6 hours at 80 ºC also leads to the formation of 33 with a yield of 81 % (Scheme 9).

The works [5, 29] are devoted to the synthesis of di- and tri-ureides of phosphoric acid from the corresponding di- and tri-isocyanate phosphates. So, in work [29], reactions of phenyl diisocyanate phosphate 34 with various amines 6.3, 6.4, 6.41–6.43 in the medium of dry benzene during boiling were investigated. At the same time, the authors said that phenyl diisocyanate phosphate 34, with long-term temperature exposure, is capable of homopolymerization — a light brown glassy homopolymer is formed — isocyanurate 35 with a yield of 30 %, which is unstable in air (Scheme 10).



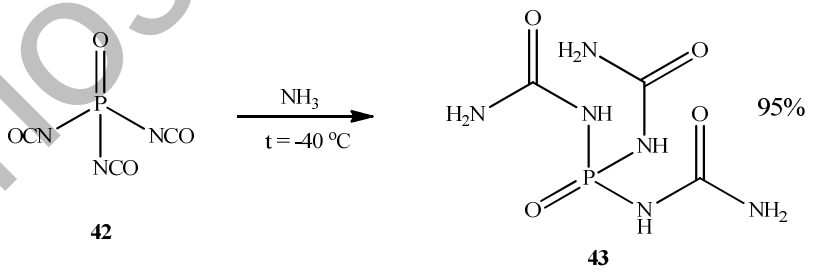
Scheme 10

Diisocyanate of benzenephosphonic acid 34 reacts with monoamines 6.3, 6.4, 6.41–5.43 to form benzenephosphonyl bis(ureas) 36.1–36.5 (Scheme 10). Products 36.1–36.5 are insoluble in benzene, carbon tetrachloride, chloroform, chloro- and fluorocarbons and ether, but they dissolve easily in polar solvents (methanol, nitromethane, acetone). Despite the fact that substances 36.1–36.5 are resistant to water and ammonia, the P–N bond is cleaved during acid hydrolysis to form phenylphosphoric acid 37 (Scheme 10).

In the reaction of phenyl diisocyanate phosphate 34 with diamines 38.1–38.4, polyureas 40.1–40.4 and 41.1–41.4 are formed in equal (1: 1) quantities, while the products of polymeric and cyclic structure are in the same reaction mass (Scheme 10). Polyureas 40.1–40.4 and 41.1–41.4 in organic solvents are insoluble, partially dissolve in dimethylformamide when heated. Also, the substances are not wetted with water and are resistant to diluted acids and alkalis.

Products 39.1, 39.2, obtained in the reaction with diamines 38.1, 38.2 in the ratio 1: 2 with prolonged heating to the melting temperature, are capable of self-condensation (Scheme 10).

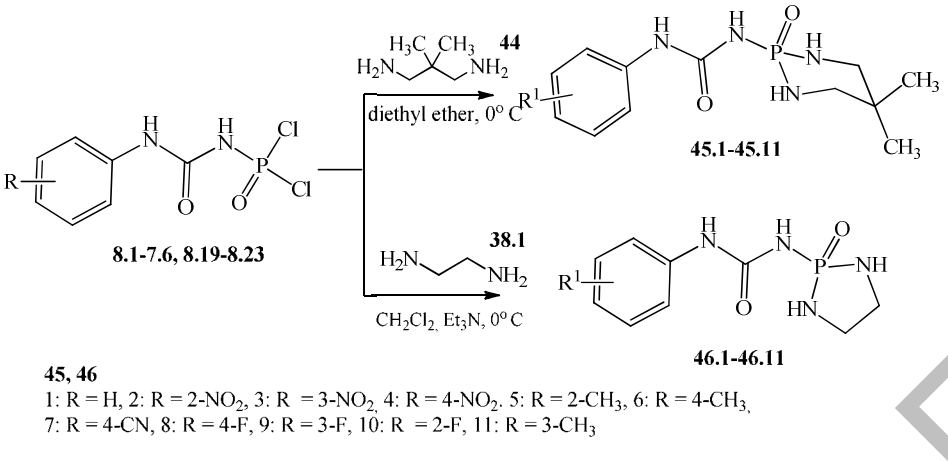
[5] reported on the synthesis of phosphorous triureide 42 by treating phosphorus triisocyanate (V) 42 with an excess of liquid ammonia at –40 ºC, and the yield of phosphorous triureide 43 was 95 % (Scheme 11).



Scheme 11

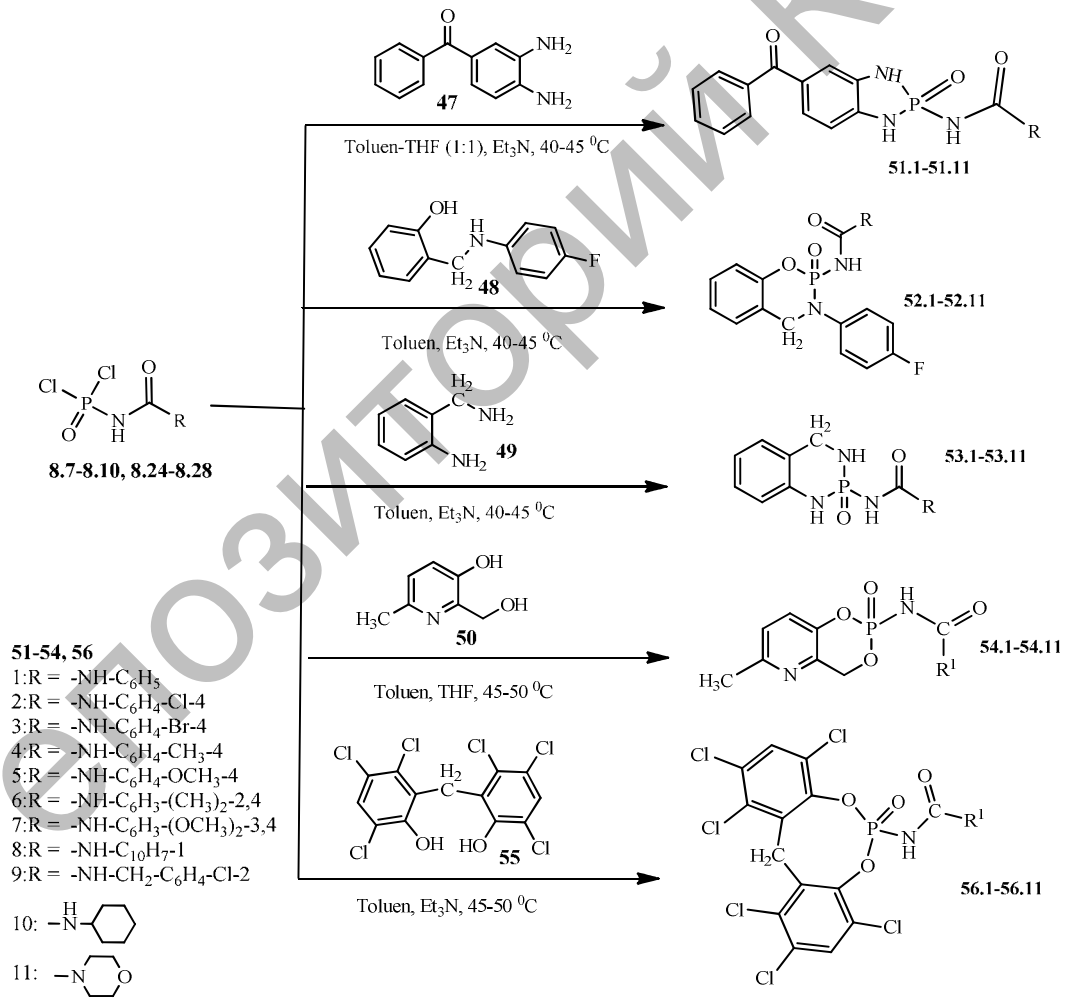
Thus, the resulting aryl carbamidophosphoric acid chlorides 8.1–8.28 using the methods described above [14–17, 21] were involved in various studies with the aim of obtaining a wide range of substances with biological activity.

The authors of [15], a series of dichlorophosphoryl derivatives of N-substituted phenylureas 8.1–8.6, 8.19–8.23, was converted to the corresponding diazaphosphorinanes 45.1–45.11 and diazaphospholanes 46.1–46.11 under the action of 2,2-dimethyl-1,3-diaminopropane 44 and ethylenediamine 38.1, respectively (Scheme 12).



Scheme 12

The synthesized dichlorophosphoryl derivatives of N-substituted phenylureas 8.7–8.10, 8.24–8.28, the authors of [18, 19], using similar methods [14, 21], were involved in condensation reactions with various diamines 47–50 to produce a wide range of compounds 51–54 based on phosphorylated ureas with antimicrobial activity (Scheme 13).

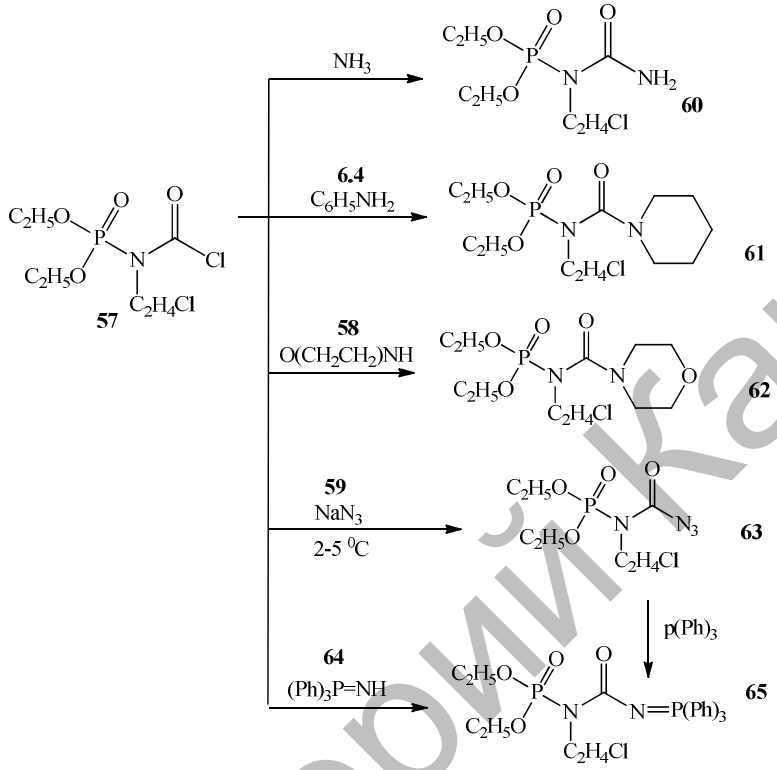


Scheme 13

In continuation of these works, later [20], by a similar reaction of condensation a number of biologically active dibenzodioxaphosphociline urea 56.1–56.11 (Scheme 13) were obtained from polychlorinated 2,2-dihydroxydiphenylmethane 55. Reactions given in Scheme 13 were carried out with weak heating in the presence of triethylamine in toluene, or in a mixture of toluene–THF (1:1) with average yields (47–71 %) for 51–54, 56.

1.2 Other methods for producing acyclic N-phosphorylated ureas

Along with isocyanates, N-dialkylphosphono-N-(2-chloroethyl)carbamic acid chloride 57 can be used as a starting phosphorylating reagent 57. The authors of [30] obtained a series of urea derivatives 60–63 by reacting N-diethylphosphono-N-(2-chloroethyl)carbamic acid 57 with ammonia, aniline 6.4, morpholine 58, and sodium azide 59 (Scheme 14):

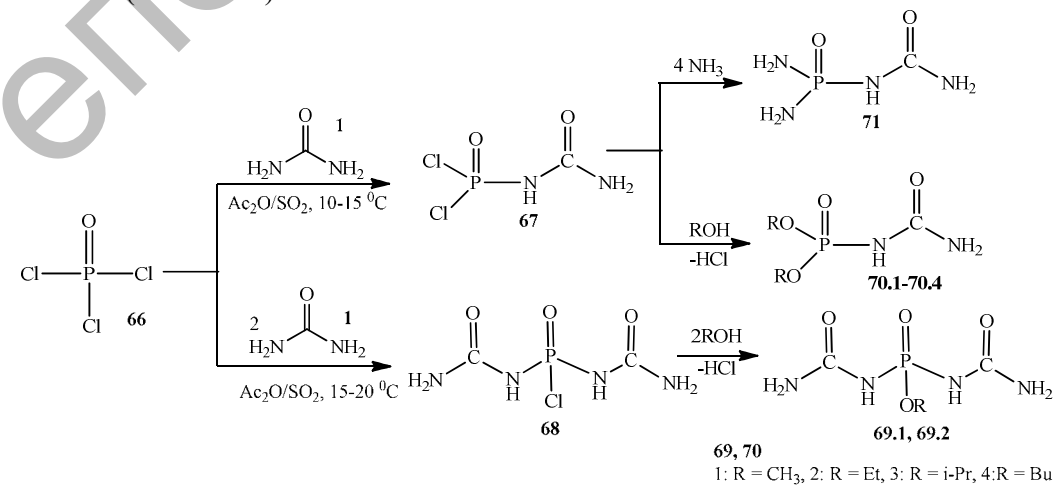


Scheme 14

N-diethylphosphono-N-(2-chloroethyl)carbamic acid chloride 57 reacts with sodium azide 59 at 2–5 ºC [30]. The phosphoazide 63 obtained in this way, like acyl azides, reacts with triphenylphosphine to form N-diethylphosphono-N-(2-chloroethyl)amidetriphenylphosphazo-carbonic acid 65, which is also obtained by reacting the acid chloride 57 with triphenylphosphoimine 64 (Scheme 14).

In the patent literature [31, 32] there are reports of the synthesis of phosphorus-substituted ureas 60–65 exhibiting nematocidal activity.

A convenient method of direct phosphorylation of urea1 was proposed [5], based on the reaction of urea 1 with phosphorus oxychloride in polar solvents, which resulted in dichlorohydrophosphoric acid 67 and diureid phosphoric acid 68 (Scheme 15).



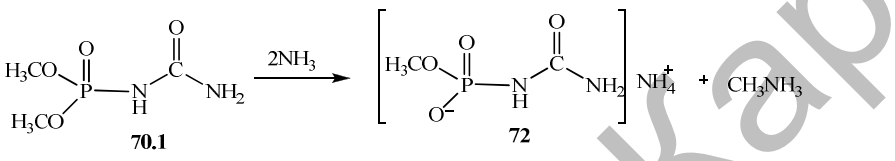
Scheme 15

It is concluded that the conditions of the process have a significant influence on the reaction. When using acetic anhydride as a solvent, the yield of 67 and 68 acids was 30 and 56 %, respectively. Replacing the solvent with liquid sulfur dioxide reduces the yield 67 significantly (30 %) (Scheme 15).

A similar method was used in [33] to obtain phosphorylated alkylureas, where the authors used a number of solvents. However, the highest yield was achieved at a molar ratio of alkyl urea: phosphorus oxychloride 66 as 4:1 in liquid sulfur dioxide.

Compounds 67 and 68 obtained were used for further reactions with alcohols to produce the corresponding esters. Reactions of ureidophosphoric acid dichloride 67 with monofunctional alcohols led to the preparation of dimethyl 70.1, diethyl 70.2, diisopropyl 70.3 and dibutyl esters of ureidophosphoric acid 70.4. It has been shown that ureidophosphoric acid dichloride 68 produced the corresponding esters 69.1, 69.2 with methanol and ethanol (Scheme 15).

It is also shown [5] that ureidophosphoric acid dichloride 67 reacts with liquid ammonia at –70 ºC with the release of white colored substance (Scheme 15). Dimethyl ester of ureidophosphoric acid 70.1, when dissolved in liquid ammonia, gives the ammonium salt of methoxouridophosphoric acid 72 (Scheme 16).

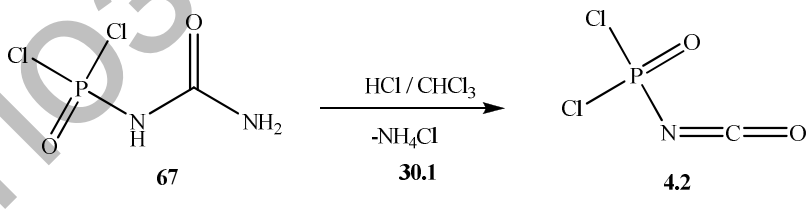


Scheme 16

Dimethyl ester of ureidophosphoric acid and phosphoroxytriureide are weak acids, prone to tautomerism, neutralization of which causes an increase in the P–N bond order (Scheme 17) [5].

Scheme 17

[34] reported that dichlorophosphorylurea 67 is almost quantitatively hydrolyzed to dichloroisocyanate phosphate 4.2 and ammonium chloride 30.1 in boiling chloroform by passing HCl (Scheme 18). This reaction takes place regardless of the nature of the substituents at the phosphorus atom (alkyl, aryl-amino) in the case of both phosphates and thiophosphates.

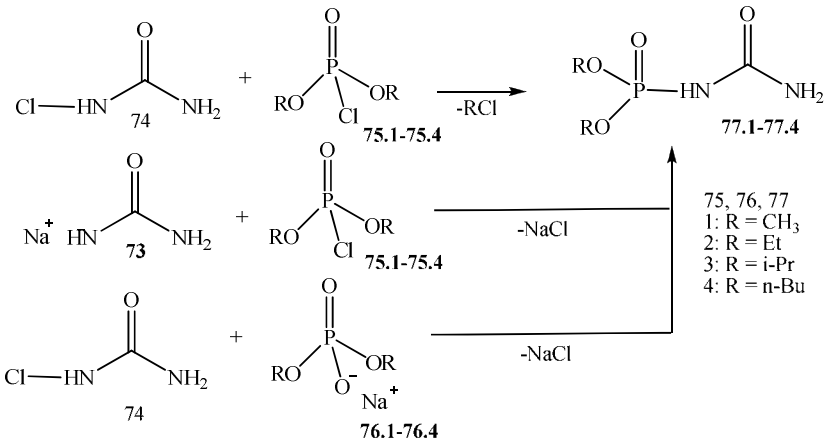


Scheme 18

It is believed [34] that the rate of isocyanate formation is consistent with differences in the electron density on the phosphorus atom, and with increasing electron density, the reaction rate increases (Scheme 18). Another way to synthesize N-phosphorylated urea is to use both the sodium salt of urea 73 and chlorine-substituted urea 74 in reactions with phosphorylating agents.

N-Chlorourea 74 and tertiary alkylphosphites 75 (methyl 75.1, ethyl 75.2, isopropyl 75.3 and n-butyl 75.4 derivatives) give ureidophosphoric esters and the corresponding alkyl halide (Scheme 19). The reaction proceeds instantly at temperatures as low as –40 ºC. Substances 77.1–77.4 are resistant to acid and alkaline hydrolysis [35].

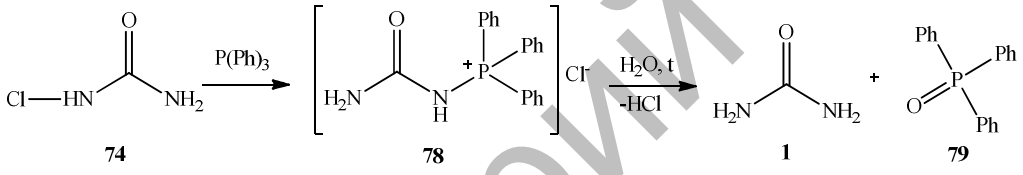
The reaction products 77.1–77.4 were confirmed by counter syntheses of N-chlorourea 74 with sodium salts of dialkyl phosphites 76.1–76.4, sodium salts of urea 73 with dialkyl chlorophosphates 75.1–75.4 (Scheme 19).



Scheme 19

In the method proposed, the reactions are carried out in an aprotic polar solvent, while the yields of the substances 77.1–77.4 obtained are 42–50 % [35].

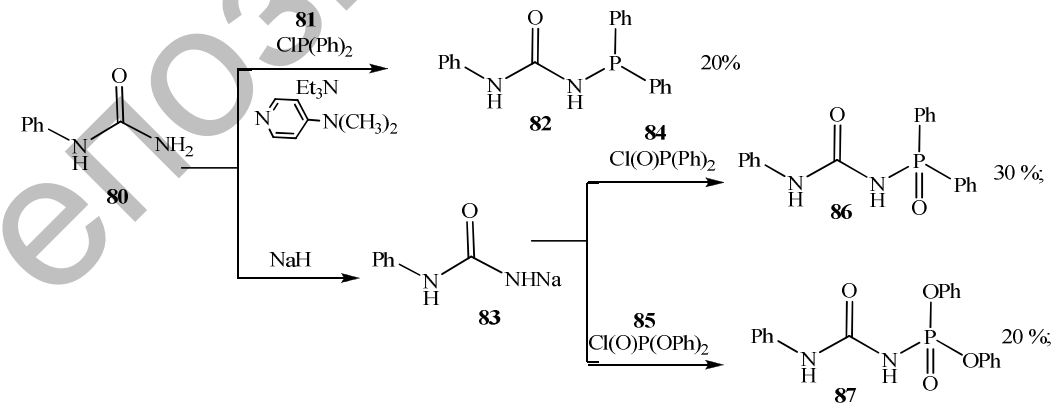
The use of triphenylphosphine as a phosphorylating component in the reaction with N-chlorourea 74, which reacts in the same way as tertiary phosphites, leads to the formation of quasiphosphonium salt 78, hydrolysis of which in warm water leads to the formation of HCl, urea 65 and triphenylphosphine oxide 79 [35] (Scheme 20).



Scheme 20

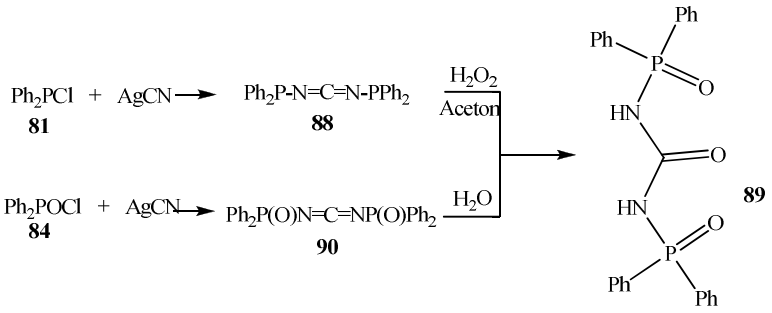
Chlorodiphenylphosphine 81 is condensed with N-phenylurea 80 in the presence of an excess of triethylamine and a catalytic amount of 4-(dimethylamino)pyridines to produce 1-(diphenylphosphinyl)-3-phenylurea 82 [36] (Scheme 21).

Also, phosphorylated ureas 86, 87 were obtained with low yields by the reaction of sodium salt of N-phenylurea 83 and phosphorus diphenyloxochloride 84 or phosphorus diphenoxyoxochloride 85, respectively [36] (Scheme 21).



Scheme 21

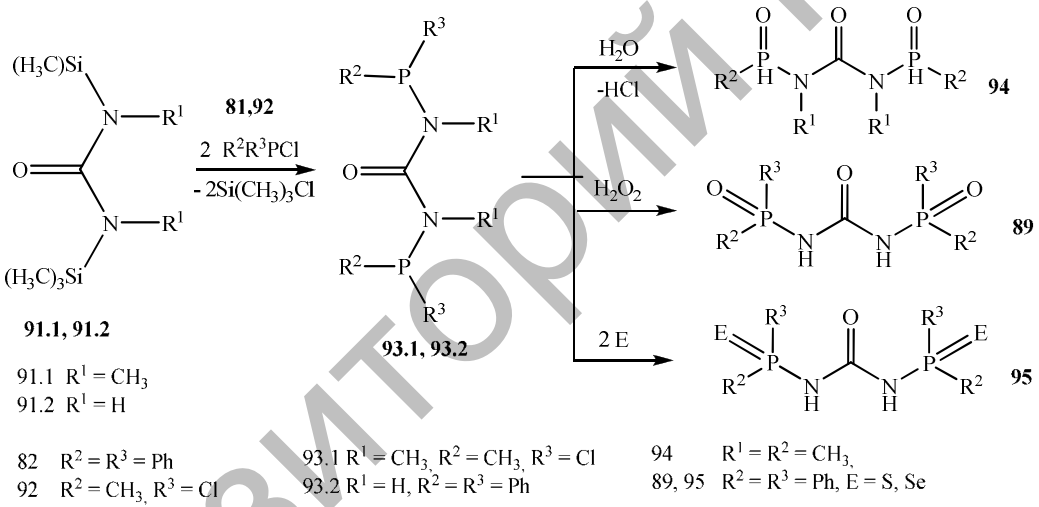
1,3-Bis(diphenylphosphoryl)urea 89 was obtained [37] by treating 1,3-bis(diphenylphosphino)carbodiimide 88, previously synthesized by the reaction of diphenylchlorophosphine 81 and AgCN, with hydrogen peroxide. The water treatment of 1,3-bis(diphenylphosphono)carbodiimide 90, obtained by the reaction of phosphorus diphenyloxochloride 84 with AgCN, leads to the same urea 89 (Scheme 22).



Scheme 22

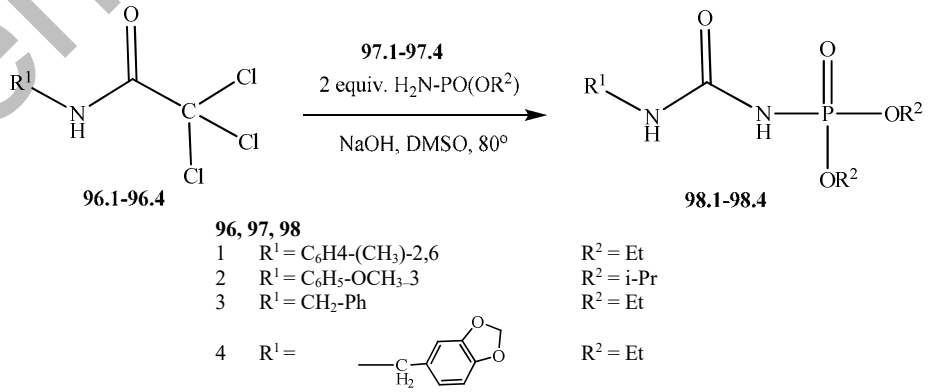
The authors of [38, 39] synthesized phosphorylated N,N'-dialkylureas 89, 94, 95 using their N,N-trimethylsilylated derivatives 91.1, 91.2 as substrates. Thus, [38] reported N,N'-bis(chloro(methyl)phosphino)-N,N'-dimethylurea 93.1 synthesis from N,N'-dimethyl-bis(trimethylsilyl)urea 91.1 and dichloromethylphosphane 92. Urea 93.1 is prone to hydrolysis with the cleavage of the chlorine atom with obtaining N,N'-dimethyl-N,N'-bis(methylhydrophosphoryl)urea 94 (Scheme 23).

In [39], it was shown that bisphosphorylated urea 93.2 is formed as a result of the reaction of diphenylchlorophosphine 81 with 1,3-bis (trimethylsilyl) urea 91.2 at 70–80 ºC. Its oxidation with hydrogen peroxide leads to the formation of urea 89, and the use of oxidizing agents (S, Se) leads to compounds of type 95 (Scheme 23).



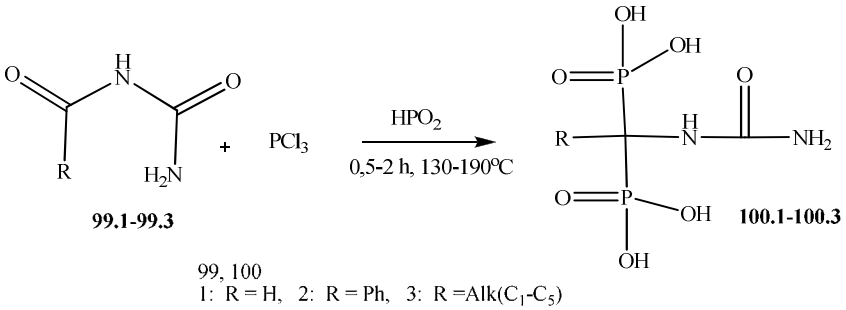
Scheme 23

The authors of [40] synthesized a series of N-phosphorylureas 98.1–98.4 by the reaction of phosphorylamides 97.1–97.4 with N-substituted trichloroacetamides 96.1–96.4 (Scheme 24).



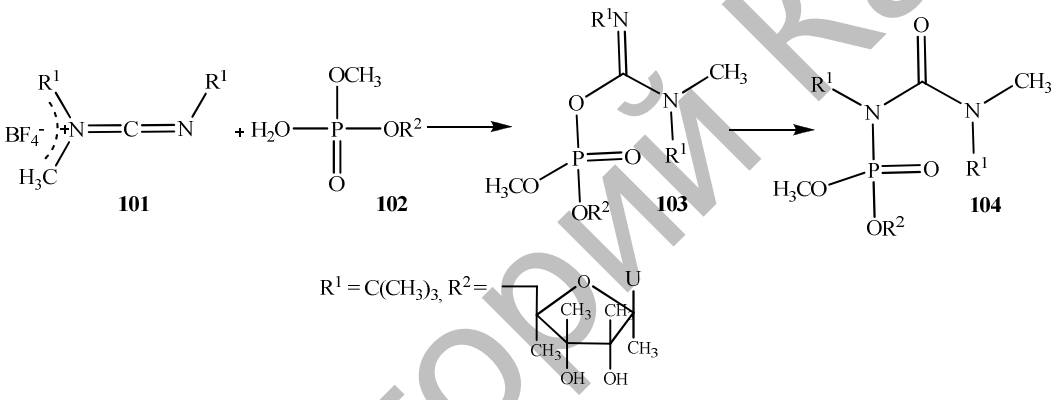
Scheme 24

The method of obtaining ureidoxyalkyl-1,1-diphosphonic acids 100.1–100.3 is described in the patent [41], which is based on the interactions formyl- 99.1, acetophenyl- 99.2, acylureas 99.3 with a mixture of phosphorous acid and PCl_3 (Scheme 25).



Scheme 25

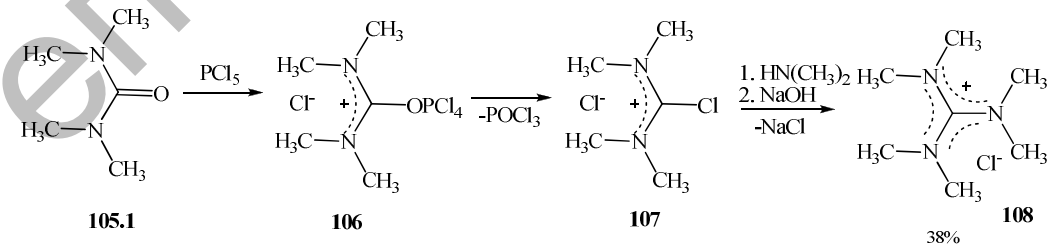
Studies [42] have shown that tetrafluoroborate-N-methyl-N,N'-di-tert-butylcarbodiimidium 101, in reaction with methyridin-5-phosphate 102, is converted to phosphorylated urea 104 through the O→N migration of the phosphate link in the intermediate compound 103 (Scheme 26).



Scheme 26

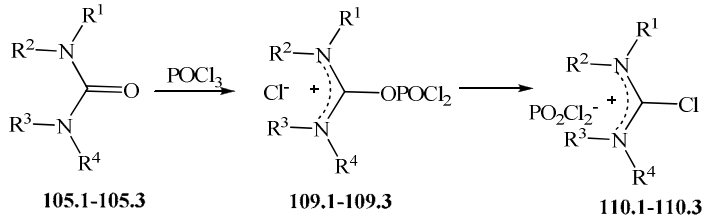
Urea's tendency to salification is interestingly used in the study of their reactions with phosphorus chlorides. Thus, during the study of the reaction of tetra-substituted ureas with various reagents, their transformations were studied, including under the action of phosphorus chlorides [43]. It was found that N,N,N',N'-tetraalkylureas 105.1–105.3 form adducts with $POCl_3$ and PCl_5.

In the reaction of phosphorus pentachloride (PCl_5) with tetramethylurea 105.1, adduct 106 is mainly formed, which turns into 107 only with increasing temperature with elimination of $POCl_3$. After alkaline treatment of 107, the reaction product is a black oil, which contains about 38 % guanidinium salt 108 (Scheme 27).



Scheme 27

It was shown that N,N,N',N'-tetraalkylureas 105.1–105.3 form adducts with $POCl_3$, which are equilibrium mixtures of imine salts 109 and 110 (Scheme 28).

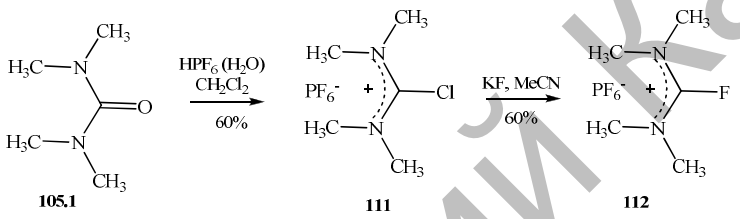


105, 109, 110
1: $R^1 = R^2 = R^3 = R^4 = CH_3$, 2: $R^1 = R^2 = R^3 = CH_3$ $R^4 = Ph$, 3: $R^1 = R^2 = R^3 = CH_3$ $R^4 = C_6H_5$-OCH_3-4;

Scheme 28

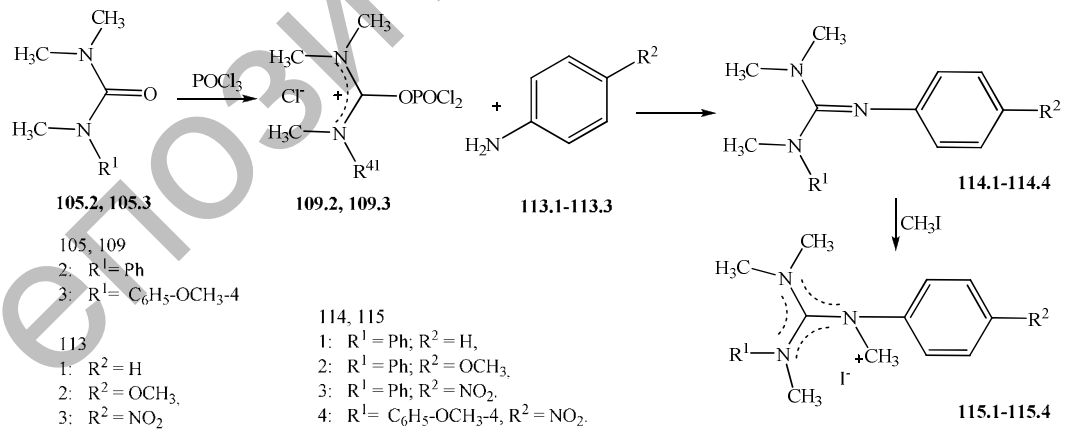
The equilibrium between urea 105.1 and $POCl_3$ in the adduct 109.1 is slow, while the equilibrium 109.1–110.1 is established quickly. The reactivity of acidic amides and ureas with respect to $POCl_3$ is in the following order: N,N-dimethylformamide > N,N-dimethylacetamide > N,N,N',N'-tetramethylurea > N,N,N',N'-tetrabutylurea [43].

The detection of adducts 109, 110 also indicates that 105.1 and HPF_6 leads to the formation of chloroformamidium hexafluorophosphate 111, which can be converted to fluoroformamidium hexafluorophosphate 112 under the action of potassium fluoride (Scheme 29).



Scheme 29

The interaction of $POCl_3$ with ureas 105.2, 105.3 in benzene (as shown earlier in scheme 28) gives equilibrium salts 109.2, 109.3. When exposed to aniline 113.1–113.3 on these salts 109.2, 109.3 and with further water-alkali treatment, you can get a mixture, consisting of urea 105.2, 105.3, guanidine 114.1–114.4 and aniline 113.1–113.3. Anilines 113.1–113.3 of the mixture can be washed out, but ureas 105.2, 105.3 and guanidines 114.1–114.4 are difficult to separate. However, pure guanidinium iodides 115.1–115.4 can be quantitatively isolated if methyl iodide is acted on (Scheme 30).



105, 109
2: R^1 = Ph
3: R^1 = C_6H_5-OCH_3-4

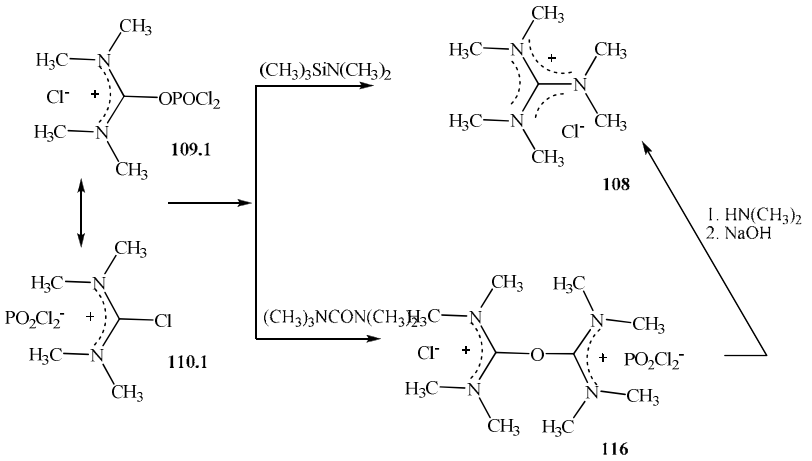
113
1: $R^2 = H$
2: $R^2 = OCH_3$,
3: $R^2 = NO_2$

114, 115
1: $R^1 = Ph$; $R^2 = H$,
2: $R^1 = Ph$; $R^2 = OCH_3$,
3: $R^1 = Ph$; $R^2 = NO_2$.
4: R^1 = C_6H_5-OCH_3-4, $R^2 = NO_2$.

Scheme 30

The authors, in their preliminary experiments, concluded that the yield of the guanidine salt 108 depends on the reaction conditions, in particular, on the molar ratio of the adducts. The guanidinium salt 108 can be obtained with a large yield by adding an excess of urea 105.1 to the iminium salts 109, 110. This may indicate the presence of other two-cationic equilibrium salts 116 in the system (Scheme 31).

The proposed ways of converting tetrasubstituted ureas with phosphorus chlorides open wide possibilities for the functionalization of the synthesized salts into new nitrogen-containing acyclic and heterocyclic compounds.



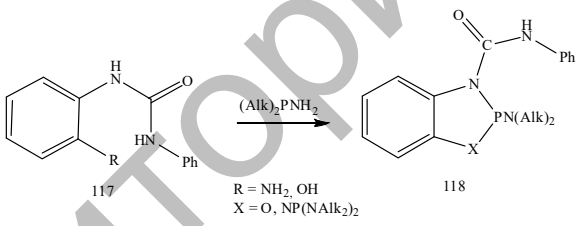
Scheme 31

Summing up this section of the review, we note that the main method for producing acyclic N-phosphorylated ureas is based on reactions that correspond to N-phosphoisocyanates with amines of various structures. Alternative methods for the synthesis of acyclic phosphazamide are represented by individual reactions, and these data are not systemic.

2 Synthesis methods of phosphorylated monocyclic ureas

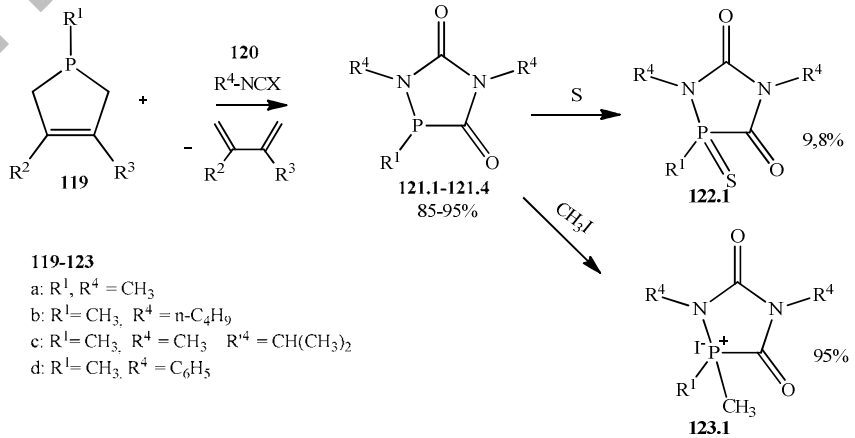
2.1 Preparation and properties of five-membered phosphorylated carbamide-containing cycles

By condensation of o-amino or o-hydroxy-substituted diphenylureas 117 with tris (dialkylamino) phosphine, the corresponding substituted 1,3,2 oxaza- and diazabenzophospholenes 118 were obtained (Scheme 32) [44].



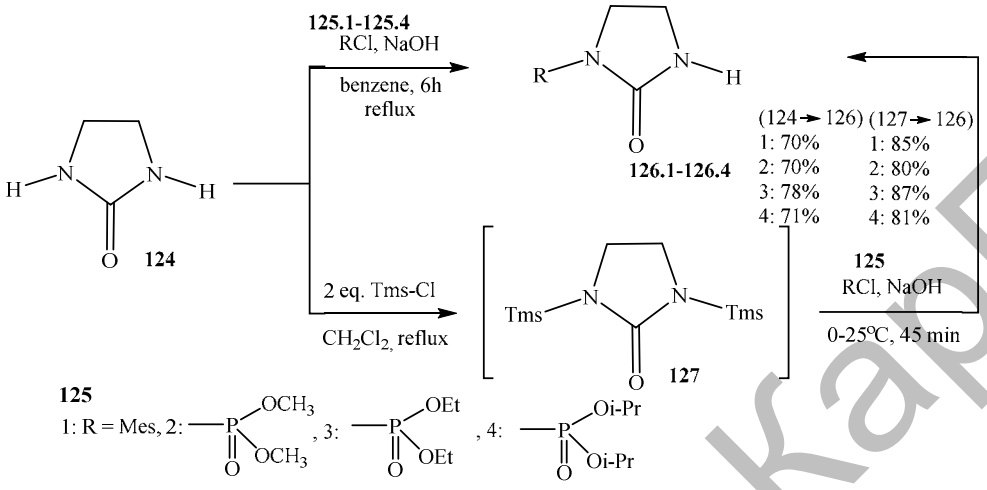
Scheme 32

A method was patented for producing 1,4,2-substituted diazaphospholidine-3,5-dione of 121.1–121.4 by the reaction of the corresponding isocyanates 120 with 1-methyl-2,5-dihydro-1H-phospholates 119 [45]. In particular, the work provides examples of the preparation of methyl- 121.1, butyl- 121.2, isopropyl- 121.3, phenyl- 121.4 derivatives of diazaphospholidine-3,5-dione, and also their modification with the production of sulfides 122 and salts 123 (Scheme 33).



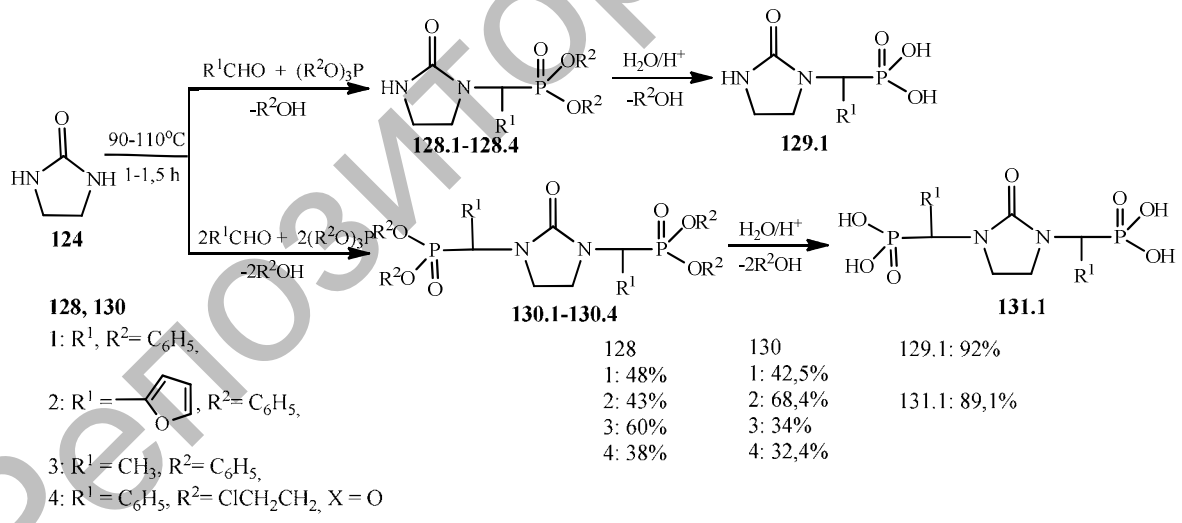
Scheme 33

It was shown that 2-imidazolidinone 124 in a strongly alkaline medium in reactions with phosphorus oxochloride esters 125.1–125.4 undergoes conversion to N-phosphorus substituted 2-imidazolidinones 126.1–126.4 with yields of 70–78 % [46]. The authors also developed an alternative pathway to compounds 126.1–126.4 with higher yields (80–87 %) via intermediate product 127 of N,N-trimethylsilylation of 2-imidazolidinone (Scheme 34).



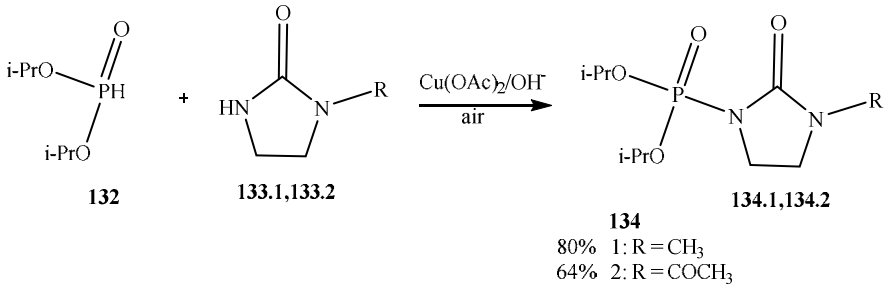
Scheme 34

It was established that the direction of the 3-component reaction of imidazolidinone 124 with aldehydes and trialkyl(aryl phosphites depends on the molar amount of the aldehyde. Thus, when using one equivalent of aldehyde and trialkyl(aryl)phosphite, 128.1–128.4 are formed, and two equivalents of aldehyde and trialkyl(aryl)phosphite in the reaction with 124 two nitrogen atoms are replaced to form 130.1–130.4. The resulting phosphoesters 128.1–128.4, 130.1–130.4 readily hydrolyze to the corresponding acids 129.1, 131.1 (Scheme 35) [47].



Scheme 35

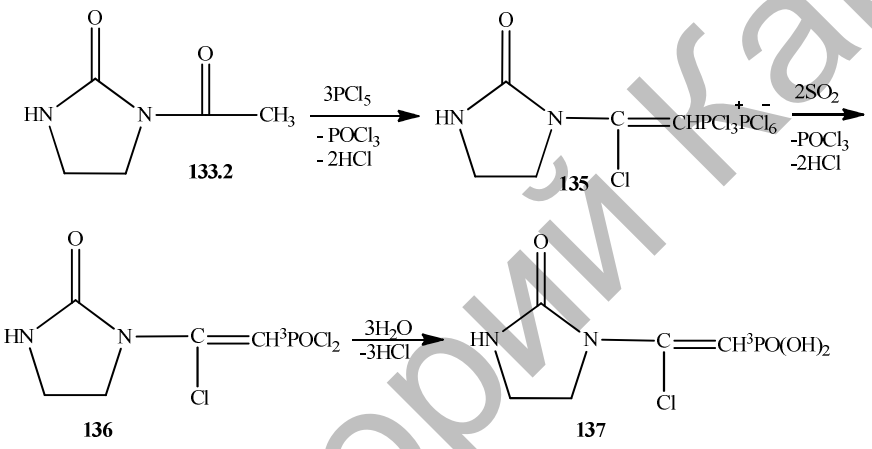
Relatively new method for the phosphorylation of organic compounds — metal complex catalysis — has been developed. As shown by the authors [48], the introduction of copper (II) acetate and the corresponding base can contribute to the occurrence of oxidative crosslinking of H-phosphonates 132 and cycloamides 133.1, 133.2 in the presence of air as the final oxidant (Scheme 36).



Scheme 36

The range of change in the amount of substrate was broad with respect to dialkyl-H-phosphonates, giving the corresponding binding products P–N 134.1, 134.2 with moderate and high yields. Among the copper catalysts studied by the authors, $Cu(OAc)_2$ showed the highest activity and selectivity.

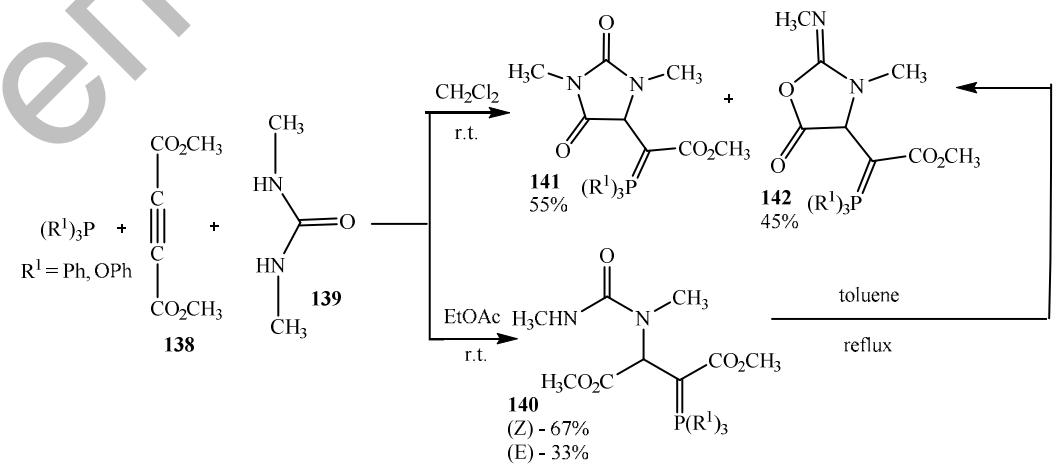
[49] studied the effect of phosphorus pentachloride on N-acetyl-N,N'-ethylene urea 133.2, which leads to the formation of 2-(2-oxo-1-imidazolidinyl)-2-chloro-ethenyltrichlorophosphonium hexachlorophosphate 135 (Scheme 37).



Scheme 37

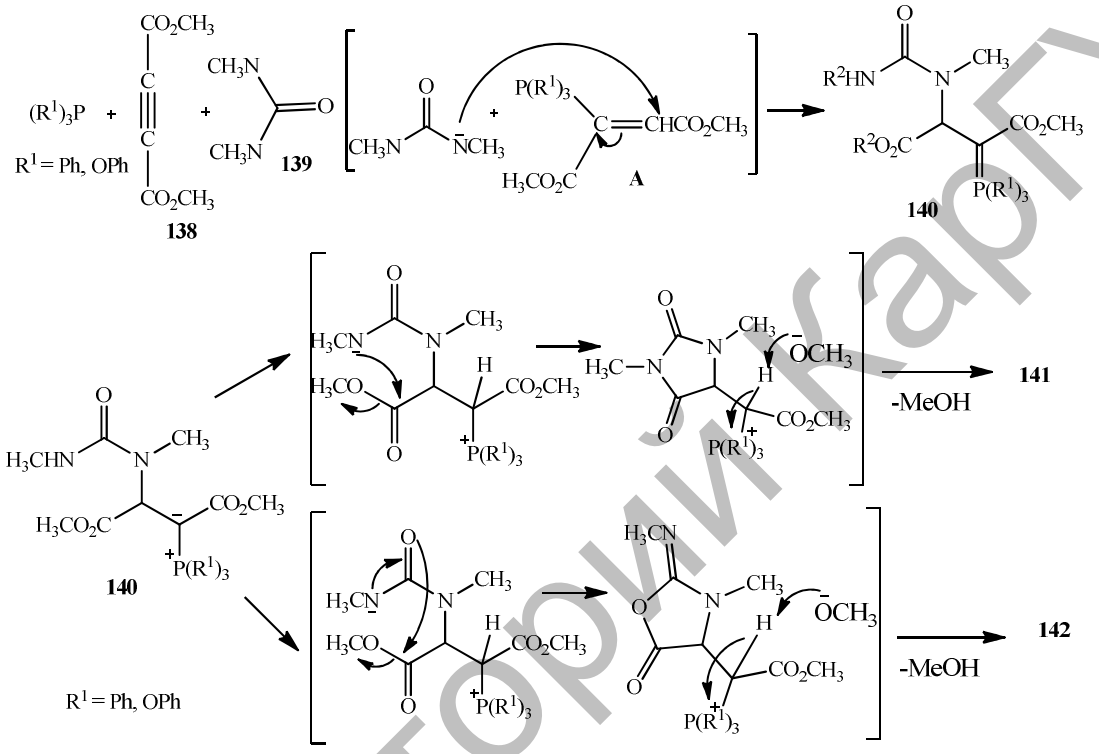
Compound 135, when treated with sulfur dioxide, is converted to 2-(2-oxo-1-imidazolidinyl)-2-chloro-ethenylphosphonic acid dichloride 136, upon hydrolysis of which 2-oxo-2- (2-oxo-1-imidazolidinyl) ethyl phosphonic acid 137 is formed (Scheme 37).

Multicomponent reactions proved to be very effective in assembling diversified molecules and searching for new ways to obtain heterocycles and organophosphorus compounds. It was reported about the reaction of compounds with the presence of three-coordinated phosphorus $(PhO)_3P$ and/or Ph_3P with dimethylacetylenedicarboxylate 138 in the presence of N,N'-dimethylurea 139 to obtain β-amidophosphonates 141, phosphonates 142, and stable phosphorus ylides 140 (Scheme 38) [50].



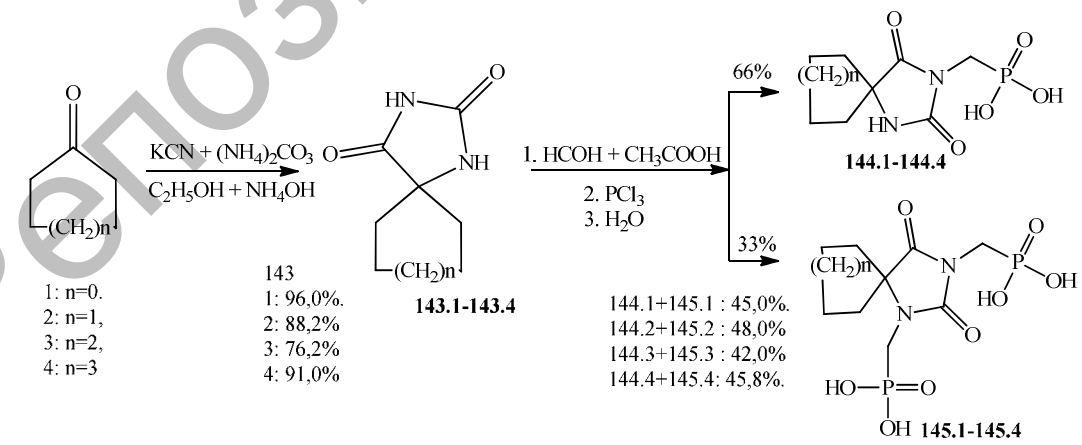
Scheme 38

This reaction (Scheme 38) was carried out in the presence of triphenylphosphine in dry dichloroethane CH_2Cl_2 as a solvent at room temperature. As a result of the reaction, hydantoin 141 and oxazolidine 142 were obtained, containing stable phosphorus ylides with good yields. Usually, the solubility of phosphorus ylides in ethyl acetate is less than in methylene chloride, therefore, the authors suggest using ethyl acetate to limit the reaction and isolate the intermediate acyclic products 140. The stepwise mechanism shown in scheme 39 is provided by a nucleophilic attack of the olefinic carbon atom of intermediate phosphoalkene by the urea anion with the formation of ureidoylide 140, the fate of which, depending on the chemistry of the process, ends with the formation of phosphorane cycles of hydantoin 141 or oxazalidinone type 142 [50].



Scheme 39

Hydantoins 143.1–143.4, previously synthesized by the Bucherer reaction [51] in the condensation reaction with formaldehyde, give regioisomers 144 and 145 in a ratio of 66 % : 33 %, respectively (Scheme 40) [10].

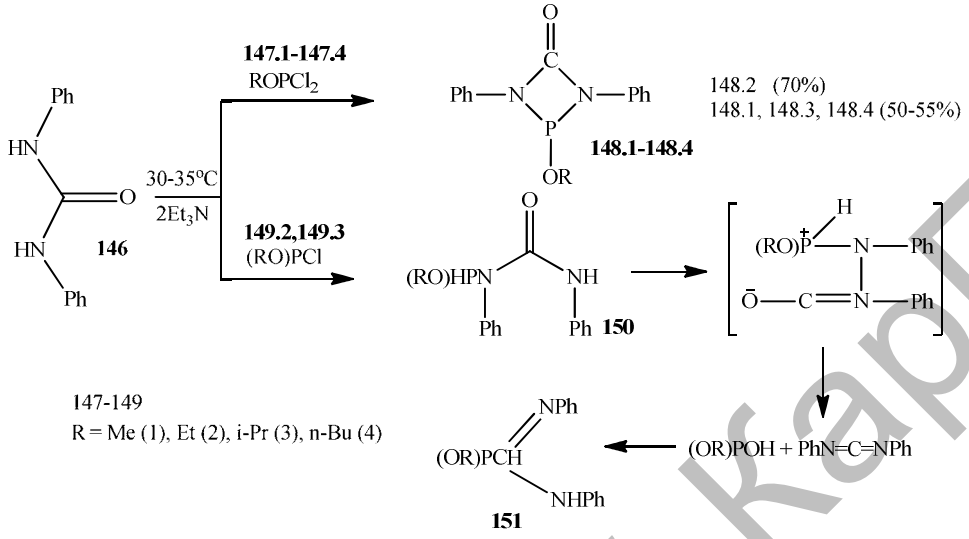


Scheme 40

2.2 Preparation and properties of tetracyclic phosphorylated urea derivatives

It has been established that the direction of urea phosphorylation reactions by ethers of chlorine derivatives of phosphoric acids depends on the coordination number of phosphorus: in the case of using a three-

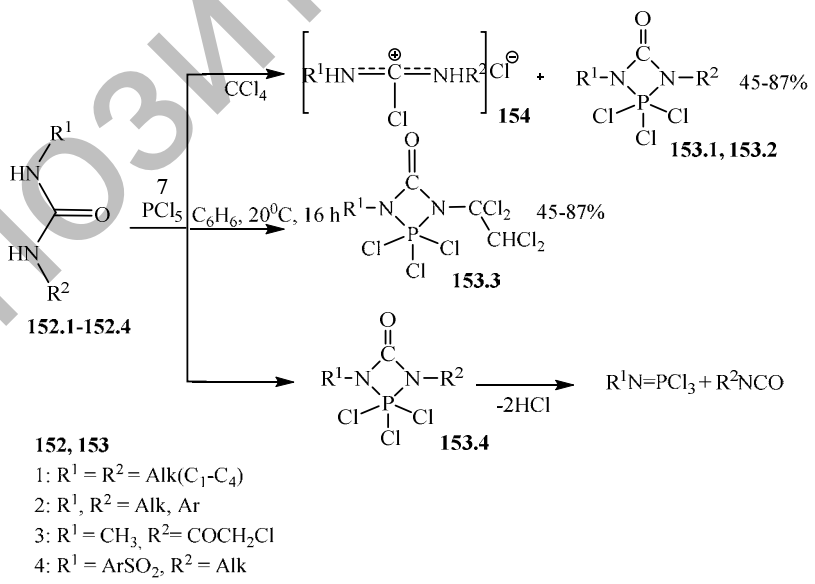
coordinated phosphorus atom, phosphorylation takes place [52]. For example, when using monoalkoxyphosphoric acid dichlorides 147.1–147.4, successful phosphazacyclization was achieved through the intermediate phosphorylation of diphenylurea 146, where the products are 1,3-diaza-2-phosphetidin-4-ones 148.1–148.4 (Scheme 41) [53].



Scheme 41

Unlike dichlorides 147.1–147.4, dialkoxyphosphoric acid monochlorides 148.1–148.2 react with diphenylurea 146 in the presence of the HCl acceptor with the initial formation of phosphorylated urea 150, which is unstable and prone to rearrangement (accelerated upon heating) into phosphorylated amidine 151 (Scheme 41). However, when using derivatives of a tetracoordinated phosphorus atom, the reaction can proceed in a different direction through the process of dehydrating diphenylurea 146 [52, 53].

Reactions of phosphorus pentachloride with 1,3-disubstituted ureas 152.1–152.2 containing primary alkyl substituents occur predominantly through the nitrogen atoms to form a four-membered cyclic structure 153.1 (Scheme 42) [54]. While ureas containing secondary alkyl groups form only minor amounts of compound 153.1, the predominant product is chloroformamidinium chloride 154 (Scheme 42) [54, 55].



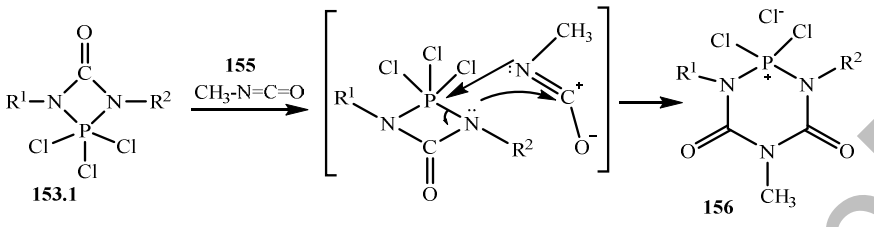
Scheme 42

Similarly, N,N'-Dialkyl(alkylaryl)urea 152.2 with phosphorus pentachloride in equimolar amounts give derivatives of trichloro-1,3,2-diazaphosphetidin-4-one 153.2 [56], although it was reported that when using an excess of PCl_5, the carbonyl group was chlorinated [56].

When N-methyl-N'-chloroacetylurea 152.3 interacts with phosphorus pentachloride, a substituted 1,2,3-diazaosphetidin-4-one 153.3 is formed [57, 58] (Scheme 42).

The effect of the structure of substituents on the nitrogen atom in urea was manifested when an attempt was made to phosphorylate 1-arylsulfonyl-3-alkyl urea 152.4. It was shown that the cyclic compound 153.4 obtained turned out to be extremely unstable (Scheme 42) [54].

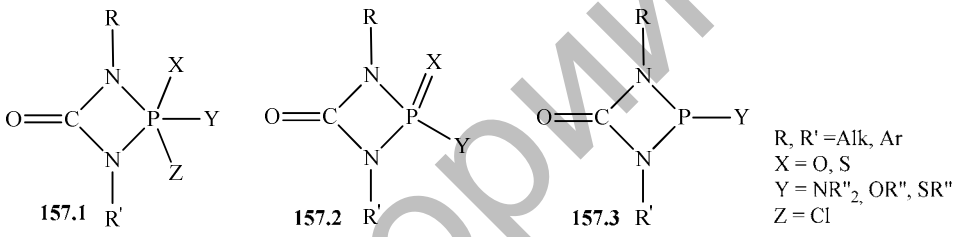
[55] reported that if methyl isocyanate 155 acts on the obtained phosphocycle 153.1, then the cycle is expanded to a 6-membered one, and the final product is isolated as a salt 156 (Scheme 43).



153. 1: $R^1 = R^2 = Alk(C_1\text{-}C_4)$

Scheme 43

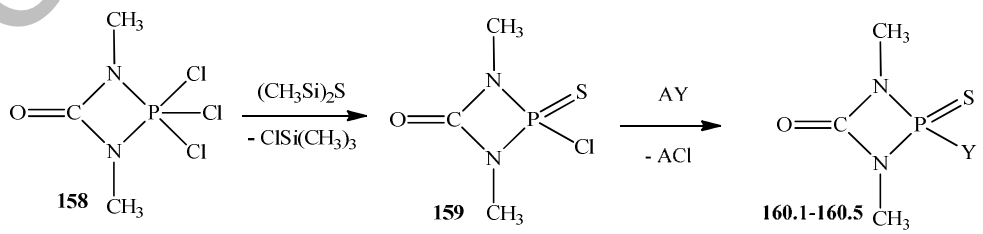
Based on previously developed convenient methods for producing diaza-2-phosphetidin-4-ones of type 153 (Scheme 42), namely, with methyl substituents (R = R '= Me) [57], aryl substituents (R, R' = Ar) [58], [59] diaza-2-phosphetidin-4-ones 157.1–157.3 were synthesized in a similar way (scheme 44) [60, 61]. The dynamic behavior of the phosphorus atom was studied by low-temperature NMR spectroscopy.



Scheme 44

By transformation with the corresponding nucleophilic reagents of phosphazacycles 153, diazaphosphetidinones of type 157 (R, R' = C) with substituents (Y = N) C_2 [62], NEt_2 [63, 64], OC [65], and CCl_3 were obtained [66].

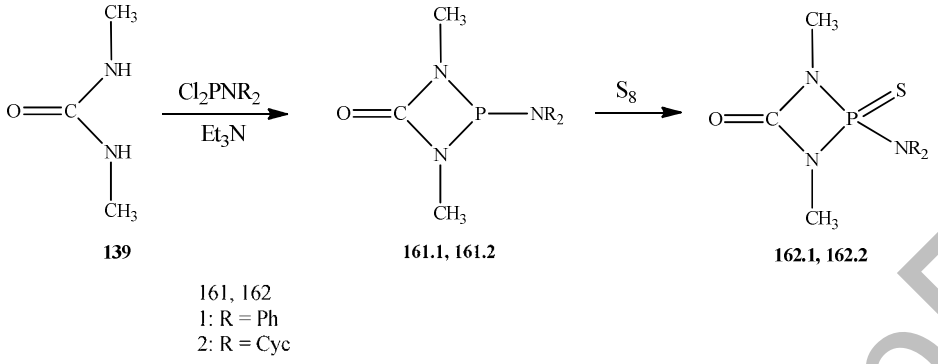
On the basis of the already studied methods for obtaining diaza-2-phosphetidin-4-ones 157.1–157.3 (Scheme 44), [67] suggested ways of converting 158 to the corresponding 2-thioderivatives 159, 160 (Scheme 45), 162 (Scheme 46). The authors report that the thio-derivatives of diazaphosphetidinone 159 can be obtained by direct oxidation of compound 158 (Scheme 45). A suitable method for the preparation of compounds 160.1–160.5 is the reaction with trimethylsilyl derivatives (AY), since the direct use of secondary amines leads to ring opening. The amino groups NR_2 (R = Me, Et, $(CH_2)_4$, OCH_3 and SCH_3) of trimethylsilyl derivatives (AY) in the reaction with 159 replace the chlorine atom, which leads to the formation of thiophosphoric acid amides 160.1–160.5 (Scheme 45).



A = H, $Si(CH_3)_3$
Y = $N(CH_3)_2$ (1), $N(Et)_2$ (2), $N(CH_2)_4$ (3), OCH_3 (4), SCH_3 (5)

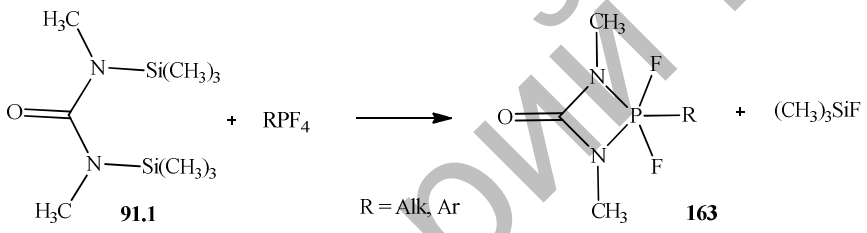
Scheme 45

However, for the synthesis of compounds 162.1, 162.2 with cyclic amine residues (NPh_2 and $N(cycl)_2$) by reacting N,N'-dimethylurea139 with the corresponding dichlorophosphorusigamide, compounds 161.1, 161.2 were obtained first, and then the phosphorus atom was oxidized with sulfur (Scheme 46).



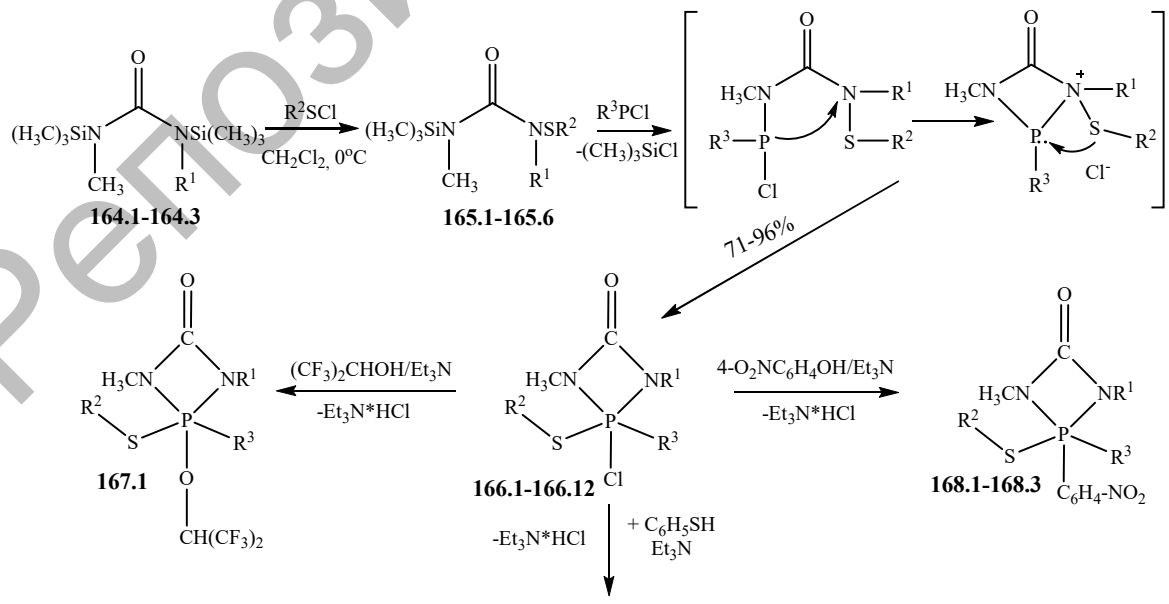
Scheme 46

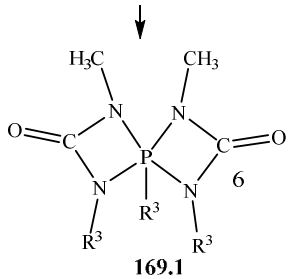
In addition, the reaction properties of 158 with respect to iso- and isothiocyanates MeNCO, PhNCO, and MeNCS were studied in [55, 68, 69]. Under the action of alkyl- or aryl-fluorophosphanes on symmetric trimethylsilyl urea derivatives 91.1, cyclization occurs with the splitting of the Si–N bond and fluorophosphadiazetinones 163 are formed (Scheme 47) [70].



Scheme 47

1-Methylsilyl-3-alkyl(aryl)sulfonyl urea 165.1–165.6, obtained from trimethylsilyl derivatives of carbamide 164.1–164.6 in reaction with aryl dichlorophosphines, cyclized smoothly to chlorophosphetidinone 166.1–166.12, which can be converted into trifluoromethyloloxy derivatives 167.1, P-aryl substituted or are subject to bicyclization to compound 169.1 [71] (Scheme 48):





169.1

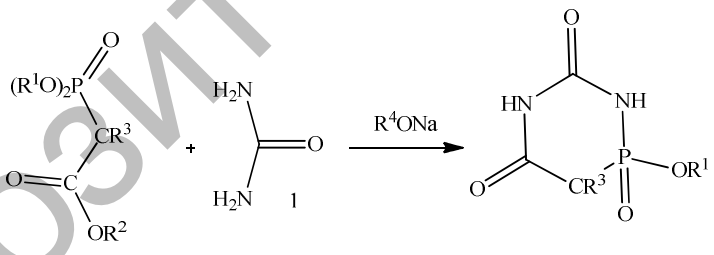
64	1: R^1 = Ph, 2: R^1 = 4-$O_2NC_6H_4$, 3: R^1 = 4-$CH_3C_6H_4$,	**166**	1: R^1 = Ph, R^2 = CH_3, R^3 = Ph; 2: R^1 = Ph, R^2 = Ph, R^3 = Ph; 3: R^1 = Ph, R^2 = CH_3, R^3 = CH_3; 4: R^1 = Ph, R^2 = Ph, R^3 = CH_3; 5: R^1 = 4-$CH_3C_6H_4$, R^2 = CH_3, R^3 = CH_3; 6: R^1 = 4-$CH_3C_6H_4$, R^2 = Ph, R^3 = CH_3; 7: R^1 = 4-$CH_3C_6H_4$, R^2 = CH_3, R^3 = CH_2Cl; 8: R^1 = 4-$CH_3C_6H_4$, R^2 = CH_3, R^3 = t-Bu; 9: R^1 = 4-$O_2NC_6H_4$, R^2 = CH_3, R^3 = Ph; 10: R^1 = 4-$O_2NC_6H_4$, R^2 = Ph, R^3 = Ph; 11: R^1 = 4-$CH_3C_6H_4$, R^2 = CH_3, R^3 = Ph; 12: R^1 = 4-$CH_3C_6H_4$, R^2 = Ph, R^3 = Ph;	87 % 92 % 87 % 90 % 94 % 85 % 90 % 71 % 91 % 96 %
165	1: R^1 = Ph, R^2 = CH_3; 2: R^1 = Ph, R^2 = Ph; 3: R^1 = 4-$O_2NC_6H_4$, R^2 = CH_3; 4: R^1 = 4-$O_2NC_6H_4$, R^2 = Ph; 5: R^1 = 4-$CH_3C_6H_4$, R^2 = CH_3; 6: R^1 = 4-$CH_3C_6H_4$, R^2 = Ph;			
167	1: R^1 = CH_3, R^2 = Ph, R^3 = Ph;	68 %		
168	1: R^1 = CH_3, R^2 = Ph, R^3 = Ph; 2: R^1 = CH_3, R^2 = 4-$CH_3C_6H_4$, R^3 = t-Bu; 3: R^1 = CH_3, R^2 = 4-$CH_3C_6H_4$, R^3 = Ph;	77 % 83 % 75 %		
169	1: R^3 = CH_3;	23 %		

Scheme 48

Thus, in this work, it is shown that the resulting phosphazacycles 167–169 are the products of nucleophilic substitution reactions of the chlorine atom in chlorophosphetidinone 166 (Scheme 48).

2.3 Preparation and properties of six-membered cycles of phosphorus derivatives of ureas

When urea 1 itself is condensed with phosphonoacetic acid esters 170.1–170.2 in the presence of sodium alcoholate, cyclic phosphoric analogues of barbituric acid 171.1–171.2 are formed (Scheme 49) [72, 73].



170.1-170.2 **170,171** **171.1-171.2**

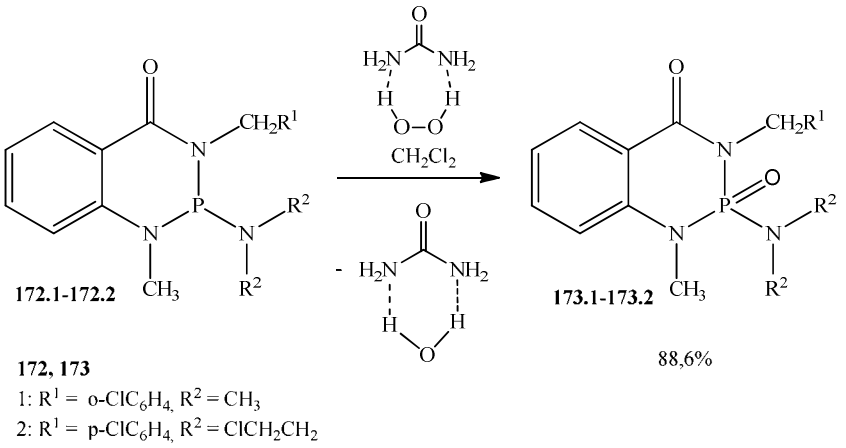
1: R^3= H_2, R^1, R^2, R^4 = Alk

2: R^3 = C_3H_5 - cycl, R^1, R^2, R^4 = Alk

Scheme 49

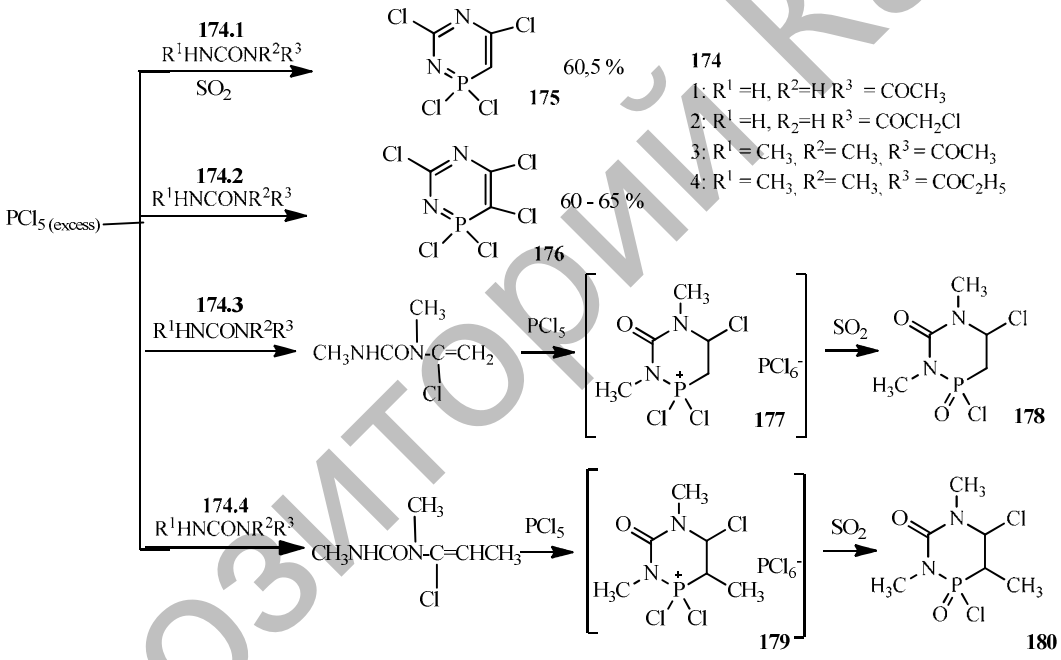
An increase in the length of the alkyl radical in phosphonic acid with an excess of sodium alkoxide can lead to spiro derivatives of barbituric acid, as it was demonstrated [73] by the example of the preparation of spirocyclopropane diazaphosphorinone 171.2 (Scheme 49).

It is curious that diazaphosphorinones 172.1–172.2 under the action of the H2O2: urea 1 complex with good yields are oxidized to phosphodiazacycles 173.1–173.2 (Scheme 50) [74], which is convenient for the conversion of aminophosphites172 into the corresponding phosphates 173.



Scheme 50

In a series of papers [8, 75–78], the processes of formation of various phosphase heterocycles based on the interaction of N-substituted acylureas 174.1–174.4 with an excess of PCl_5 were studied (Scheme 51).



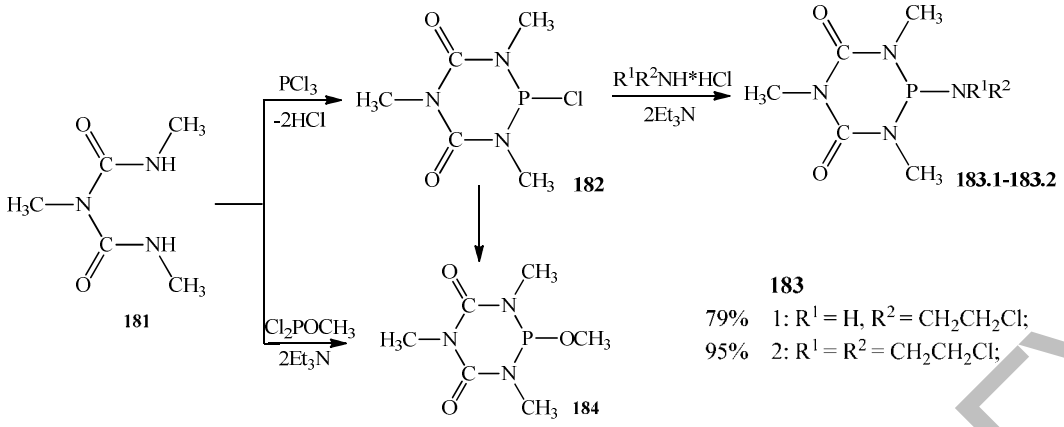
Scheme 51

It has been proved [75–77] that the cyclization of N-acetylurea 174.1 under the action of a fivefold excess of PCl_5 occurs with the participation of the acetyl group and the amino group to form trichlorophosphate heterocycle 175 (Scheme 51).

Chloroacetylurea 174.2 when heated with phosphorus pentachloride forms diazophosphorin 176, which differs from compound 175 in that in this case one more proton is replaced by a chlorine atom [78] (Scheme 51).

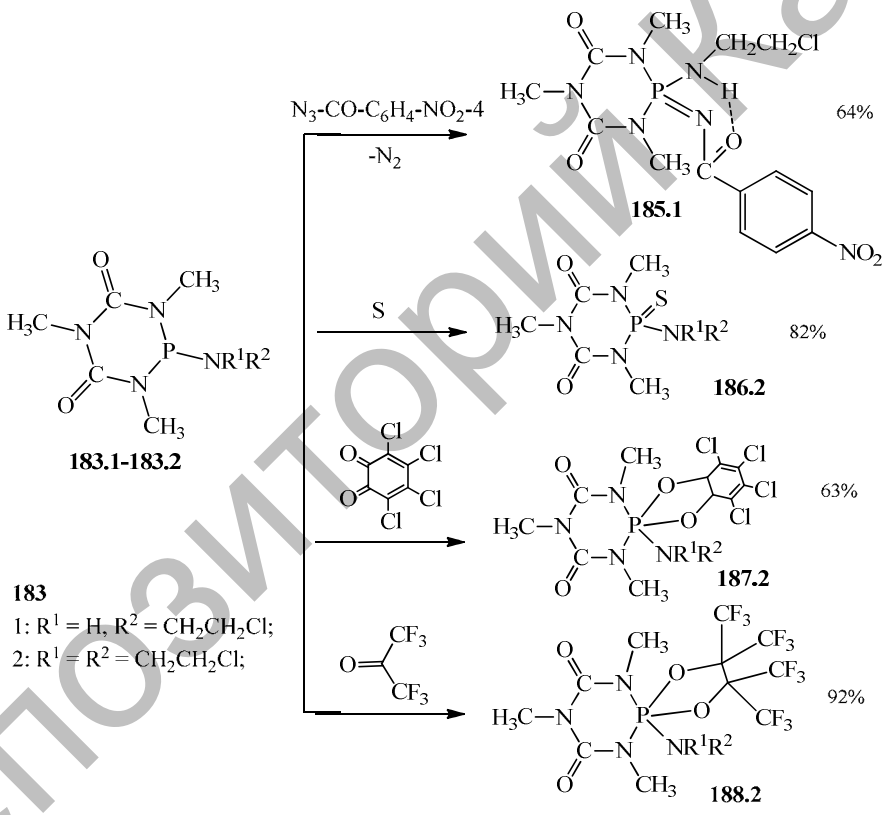
When N,N'-dimethylacetylureas 174.3–174.4 interact with phosphorus chloride in a 1:5 ratio, diazaphosphorionic salts 177, 179 are formed, which are in situ transformed into diazaphosphorins 178 and 180, respectively [8] when treated with SO_2 (Scheme 51).

A method for the synthesis of 1,3,5-triaza-2-phosphorinanediones 182, 183.1–183.2 was developed [79]. containing the carbamide moiety in the cycle, by reacting PCl_3/Cl_2POCH_3 and 1,3,5-trimethylburet 181 (Scheme 52), the methoxy derivative 184 is obtained from the chlorine derivative 1,3,5-triaza-2-phosphorinanedione 182 [80].



Scheme 52

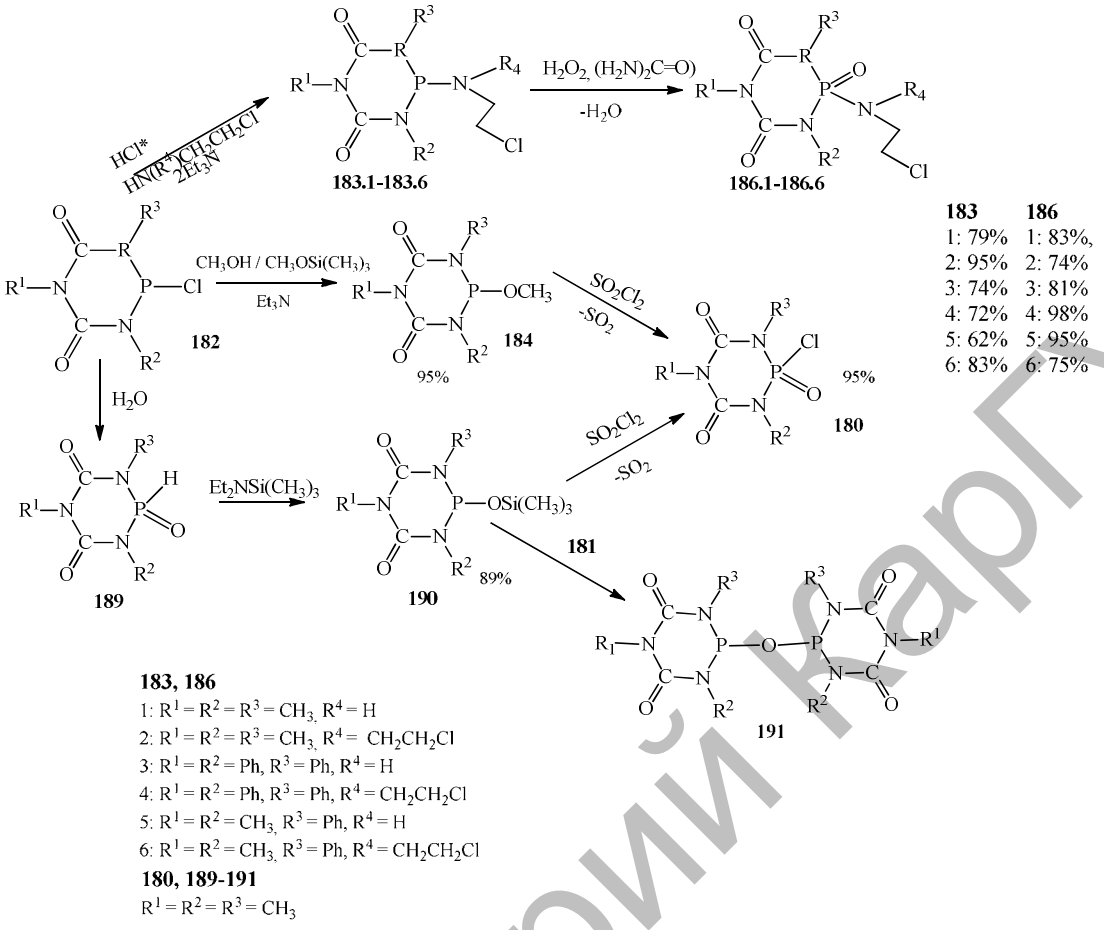
In the same work [79], the authors studied some of the chemical properties of 183.1–183.2, where, in diagram 53, the following processes were demonstrated for 183.1–183.2: oxidative ammonolysis (compound 185.1, sulphidation (compound 186.2), oxycyclization (compounds 187.2 and 188.2).



Scheme 53

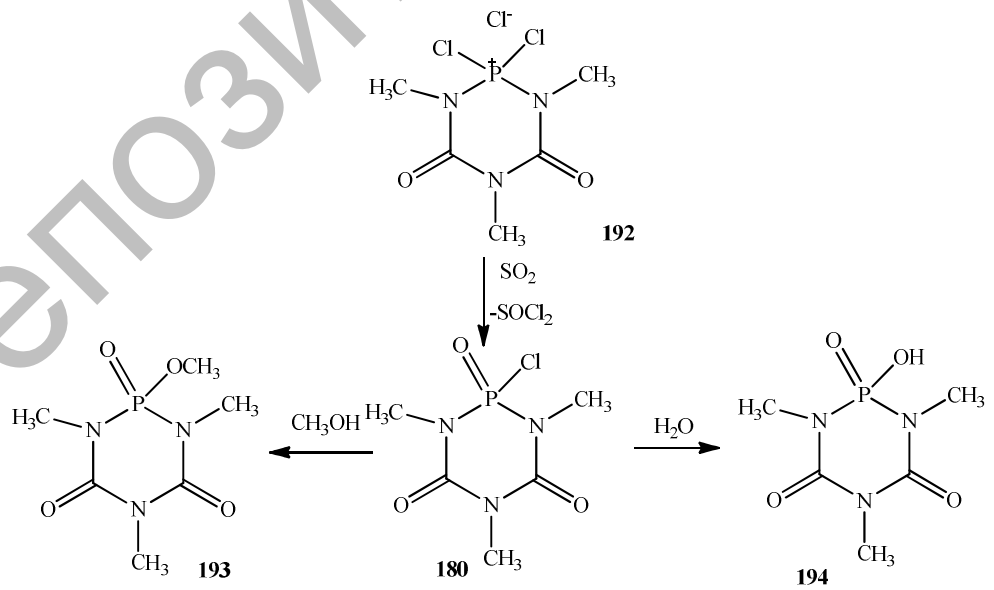
In subsequent reports [80–82] the authors involved the synthesized 1,3,5-triaza-2-phosphorinanediones 182–184 in a wide range of chemical transformations 180, 186–201 (Schemes 54–57).

Scheme 54 reflects the reactions of 1,3,5-triaza-2-phosphorinanediones 182–184 [80]: oxidation (compounds 186.1–186.6), hydrolysis (compound 189), oxidative chlorination (compound 181), which proceeds through an intermediate salt formation 192 [55] (Scheme 55), silylation (compound 190) and esterification (Compound 191) (Scheme 54).



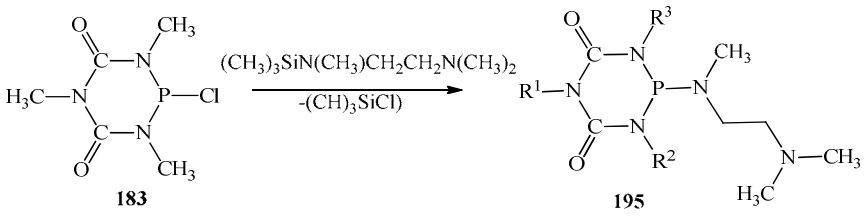
Scheme 54

When exposed to SO_2 gas on a 6-membered cycle 192, the latter is able to take a more stable form 180, capable in further interactions to easily exchange the chlorine atom for the OH and OCH_3-group under the action of water or methanol to produce products 193, 194 (Scheme 55) [55].



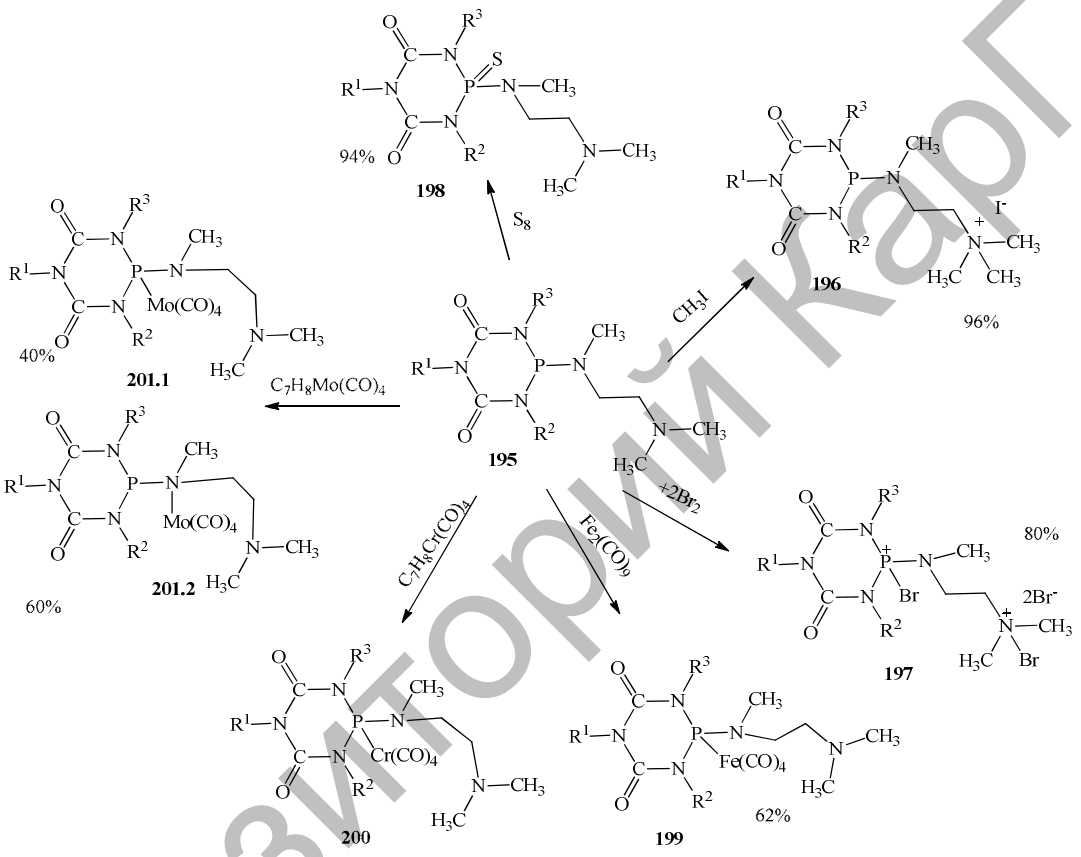
Scheme 55

Scheme 56 shows the process of exchanging the chlorine atom of the cyclic compound 182 for an amino group with the production of the diamine derivative 1,3,5-triaza-2-phosphorinane-dione 195 [82].



Scheme 56

Scheme 57 shows various variants of modification of compound 195, carried out in [82] and leading to the formation of the corresponding salts 196, 197, sulfide 198, and complex compounds 199–201.



Scheme 57

The demonstrated path of transformation of the phosphazacycle 195 using simple and accessible reagents serves as an illustrative example of the possibility of synthesizing a variety of phosphazaheterocycles that have a wide potential for their practical application.

Thus, an analysis of the available literature data on the methods of synthesis and properties of phosphorylated monocyclic carbamide-containing compounds suggests that the five-membered cycles in the vast majority are represented by imidazolidine structures 124, 126, 128–131, 134–137, 141, 144, 145, containing phosphorylated groups in the side chain, with the exception of individual imidazolidines containing a phosphorus atom in the cycle (diazabenzophospheneum 118 and diazaphospholidinedione 212.1.1–121.4).

The formation of tetracyclic phosphorylated ureas by corresponding reactions leads only to diazaphosphetidinones with the three-coordinated phosphorus atom 148, 161, and with the five-coordinated phosphorus atom in the cycle as well 153, 158–160, 162, 163, 166–168.

The formation of six-membered phosphorylated urea-containing azacycles is mainly come down to diazophosphorins 175, 176, 178, 180 and triazaphosphorinanionones 182–201, although there are some cases of synthesis of phosphoric analogues of barbituric acid 171.1–171.2.

A curious observation is the ability of transformation of four-membered diazaphosphetidinones into six-membered triazaphosphorinanionones (Scheme 43).

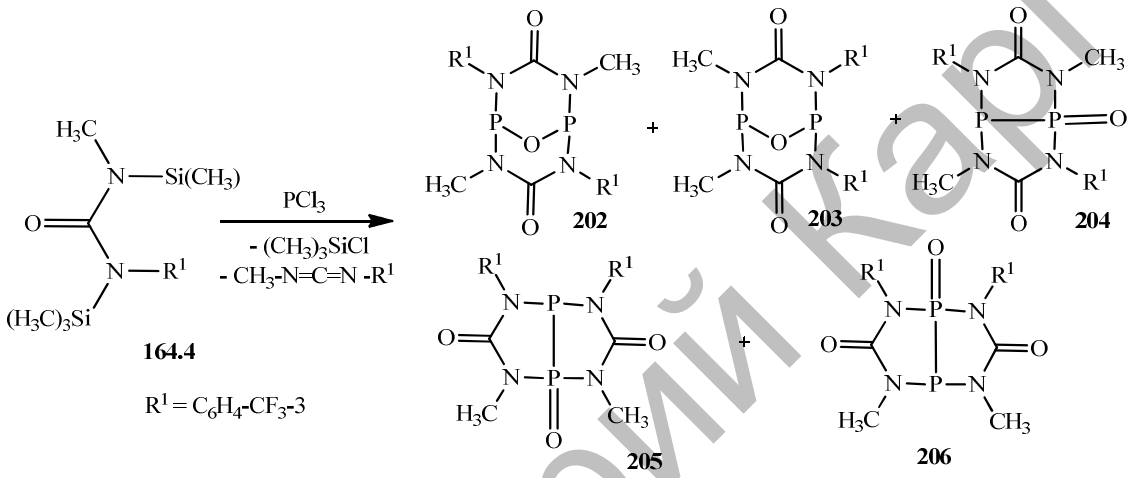
3 Synthesis methods of phosphorylated bicyclic bisureas

3.1 Bicyclic bisureas with diphosphate[3,3,0]-3,7-dione structure

An analysis of the literature data showed that 1,3-bis(trimethylsilyl)urea and its derivatives (91, 164) were often used to construct heterocyclic compounds. The attractiveness of the latter is determined by the fact that they turned out to be very convenient synthons for building a number of phosphorus-containing bicyclic bromides 202–209, 212, 213 (Schemes 58–60).

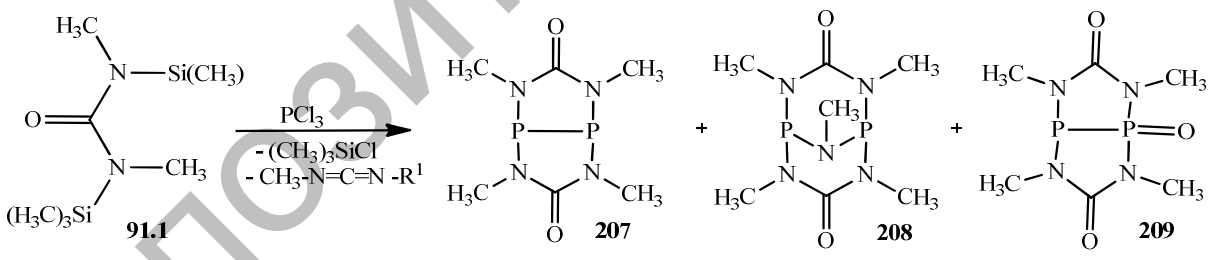
Thus, bis(trimethylsilyl)urea 164.4 was used by the authors [83] in reactions with PCl_3, where the product was cyclo[3,3,1]nonane-3,7-dione 202 (41 %). At the same time, carbodiimide 3-$CF_3C_6H_4$–N=C=N–CH_3 was released as a by-product in the reactions (Scheme 58).

In other studies, the authors of [84], by varying the conditions of the process of phosphorylation reaction 164.4 with PCl_3, found that in a similar reaction 164.4 with PCl_3 individual substance 202 was not formed, but a series of bicyclic diuretic [3,3,0]-3,7-dione structures 202–206 with nodal P–P bond (Scheme 58).



Scheme 58

In extension of their research, the authors [84] studied the reaction of 1,3-dimethyl-1,3-(trimethylsilyl)urea 91.1 with PCl_3, where it was also noted that in addition to the target product 207, compounds 208, 209 are obtained as well (Scheme 59).



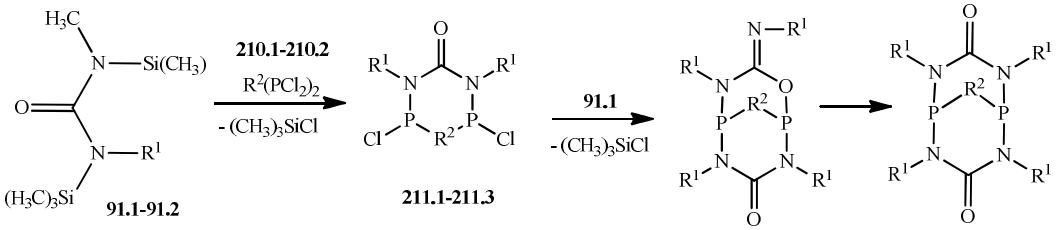
Scheme 59

It was found [85] that the reaction of methylsilyl urea 91.1 with methylenediphosphodichloride 210.1 in an inert atmosphere is completed by bicyclization to diphosphate[3.3.1]nonan-3,7-dione 213.1 and 213.2, respectively, while the reaction of urea 91.2 with dichloromethylene di-phosphodichloride 210.2 proceeds with the formation of dichloro-derivative diphosphate[3.3.1]nonan-3,7-dione 213.3 (Scheme 60).

It is postulated that these reactions proceed through intermediate monocycles 211.1 and intermediates 212.1, which regroup to thermodynamically more stable products 213.1 [86] (Scheme 60).

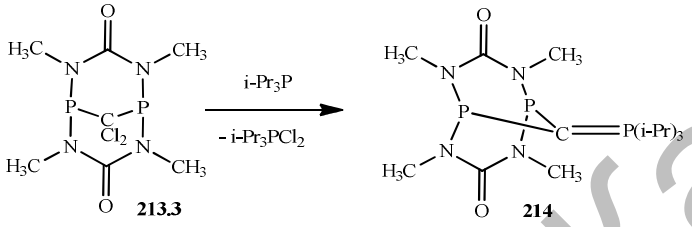
Dichloro derivative diphosphate[3.3.1]nonan-3,7-dione 213.3 reacts nucleophilic substitution with triisopropylphosphine, which, as expected, led to C-phosphine substituted ylide 214, (Scheme 61). Bicyclic ylide 214 was detected by deciphering ^{31}P NMR spectra, but was not isolated due to low stability [86].

The properties of bicyclic bisureas 205, 207, and 209 were studied in [84, 86–88].



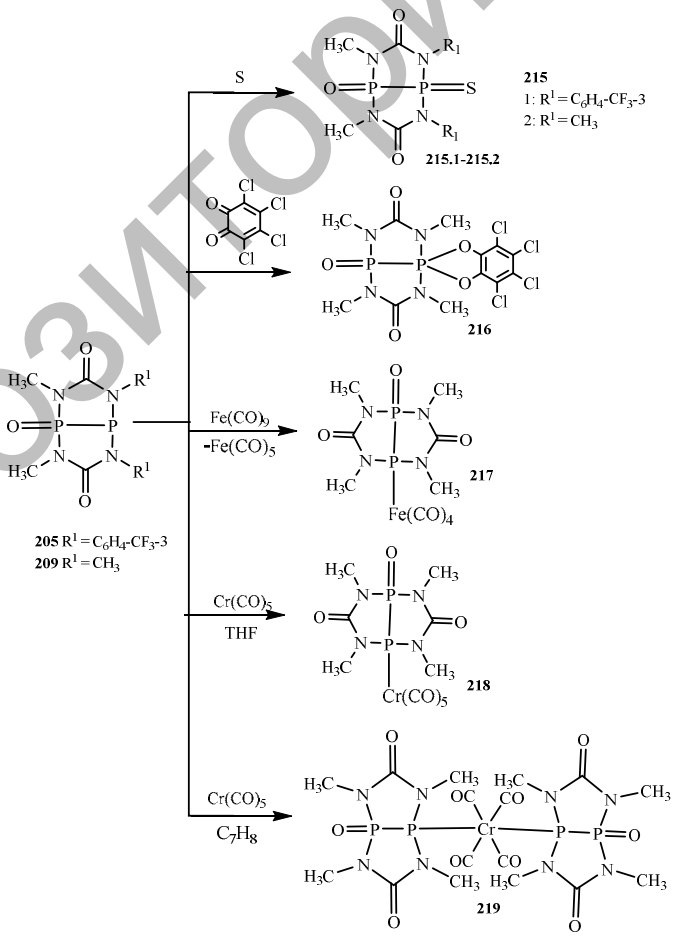
91 1: $R^1 = CH_3$, 2: $R^1 = H$ **210** 1: $R^2 = CH_2$ 2: $R^2 = CCl_2$ **211, 212, 213** 1: $R^1 = H$, $R^2 = CH_2$ 2: $R^1 = CH_3$, $R^2 = CH_2$ 3: $R^1 = CH_3$, $R^2 = CCl_2$

Scheme 60



Scheme 61

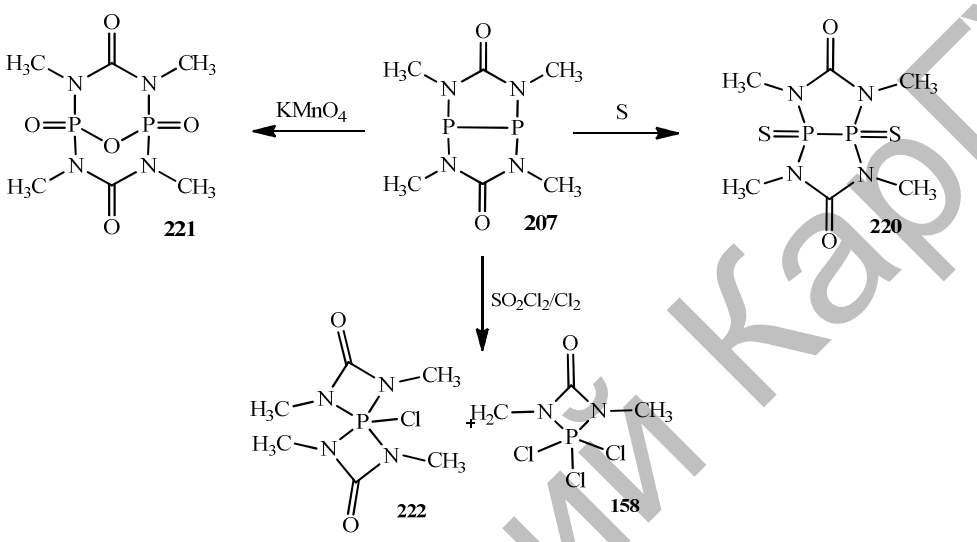
Compounds 205, 207, and 209, when interacting with elemental sulfur, tend to form a P=S bond in bicycles 215.1–215.2, 220 (Scheme 62, 63) [87]. It was also found that compound 209, in turn, readily reacts with hexachlorobenzene to form a modified cycle 216, which is a colorless solid, melts at 204–206 ºC, is sensitive to hydrolysis and is easily soluble in CH_2Cl_2 and toluene (Scheme 62) [88].



Scheme 62

In the course of further study of the properties of phosphazabicycle 209, complexes 217–219 with $Fe_2(CO)_9$ and $Cr(CO)_5$ were isolated and studied. Complexes 217, 218 are obtained in a molar ratio of 1:1. Complex 219 is obtained in the reaction with a ratio of 2:1 phosphorus derivative 209 (o) $Cr(CO)_4C_7H_8$, respectively.

During the oxidation of a phosphazabicycle 207 by potassium permanganate, the phosphorus in the P–P node of the bicycle is oxidized to the pentavalent state with the formation of a P–O–P bridge in compound 221 (Scheme 63) [87]. Further study of the properties of the phosphazabicycle 207 showed that the treatment of the latter with 207 molecular chlorine or SO_2Cl_2 leads to the formation of a mixture of phosphetidinone 158 and a spirocycle 222 with a P–Cl bond (Scheme 63) [84].

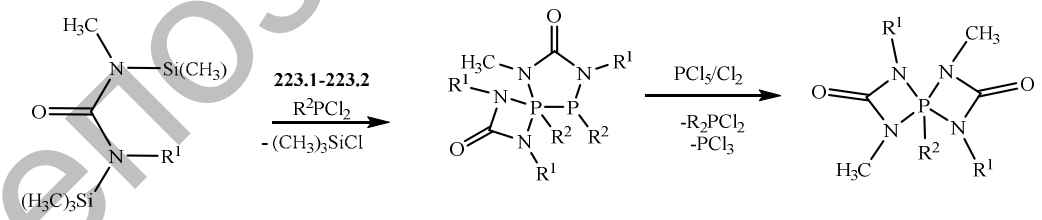


Scheme 63

To identify specific interactions of the phosphazabicycle 207, the ability of complex 207 to complexation with $Cr(CO)_5$ was shown in [84]. Thus, in the works [84, 86–88], bicyclic di-phosphate[3,3,0]-3,7-dione structure 202–209, 212–222 synthesized on the basis of bis(trimethylsilyl)urea 91, 164 were obtained and studied.

3.2 Bicyclic bisureas with difosfaspiro[3,4]octane-2,7-dione structure

[89] reported that the participation of 2 molecules of 1,3-bis(trimethylsilyl)urea 91.1, 91.2, 164.1, 164.7 in reactions with two molecules of dichloro(aryl)phosphanes 223.1–223.2 leads to bicyclization to tetraazadifosfaspiro[3, 4]octane-2,7-dyons 224.1–224.3 with a fairly good yield (87 %) (Scheme 64).



91
1: $R^1 = CH_3$,
2: $R^1 = H$
164
1: $R^1 = C_6H_5$,
4: $R^1 = C_6H_4\text{-}CF_3\text{-}3$,

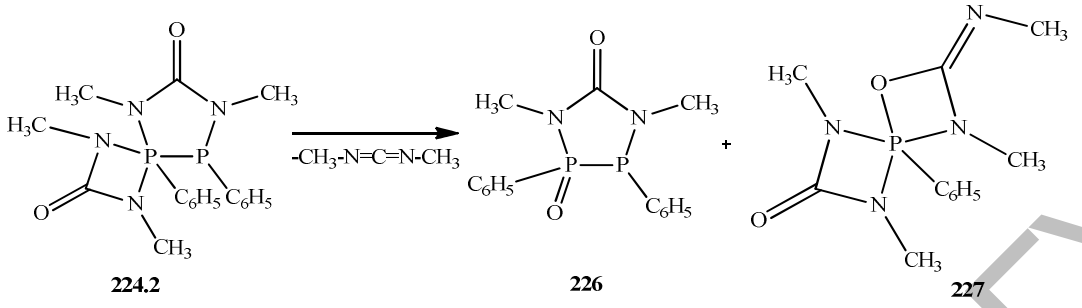
223
1: $R^2 = C_6F_5$
2: $R^2 = C_6H_5$

224, 225
1: $R^1 = C_6H_4\text{-}CF_3\text{-}3$, $R^2 = C_6F_5$
2: $R^1 = CH_3$, $R^2 = C_6H_5$
3: $R^1 = C_6H_5$, $R^2 = C_6H_5$

Scheme 64

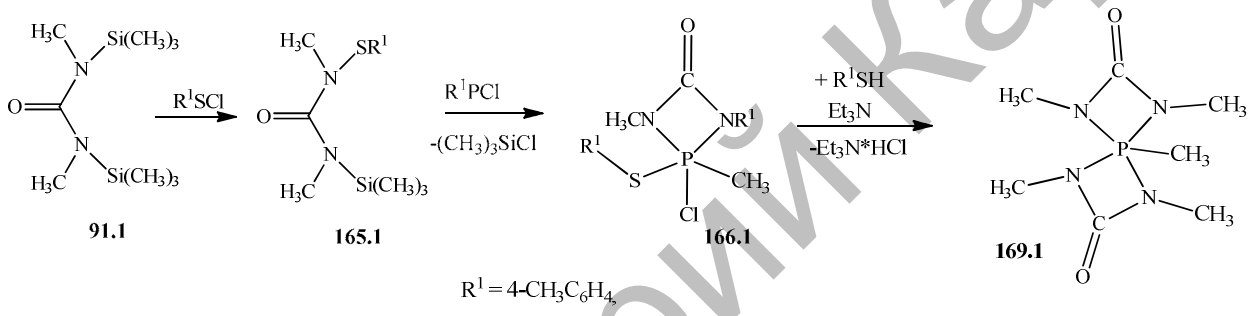
Further, when studying individual chemical properties of 224.1–224.3, it was established [83] that when exposed to molecular chlorine or PCl_5, [3,4]-octane cycles 224.1–224.3 are converted into [3,3]-heptane cycles 225.1–225.3 (Scheme 64).

In the process of studying the properties of spirobicyclic compounds, compound 224.2 was pyrolyzed, which contributed to the narrowing of its cycle to diazaphospholidin-5-one-2-oxide 227, through the formation of an intermediate monocycle 226. In this case, the corresponding carbodiimide is eliminated (Scheme 65) [87].



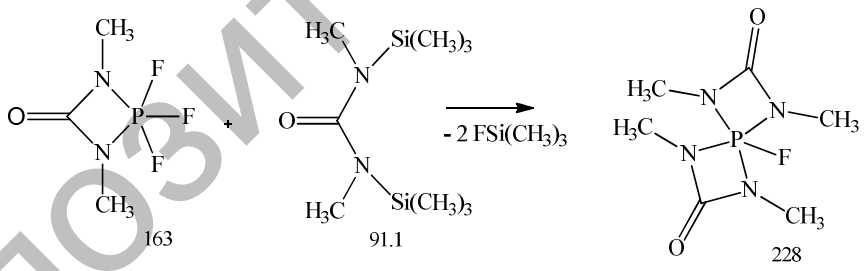
Scheme 65

1-Methylsilyl-3-alkyl(aryl)sulfonyl urea 165.1, previously prepared from trimethylsilylcarbamide derivative 91.1 in reaction with aryl dichlorophosphines, is cyclized to form a bicycle 169.1 through the formation of chlorophosphetidinone 166.1 (Scheme 66) [72].



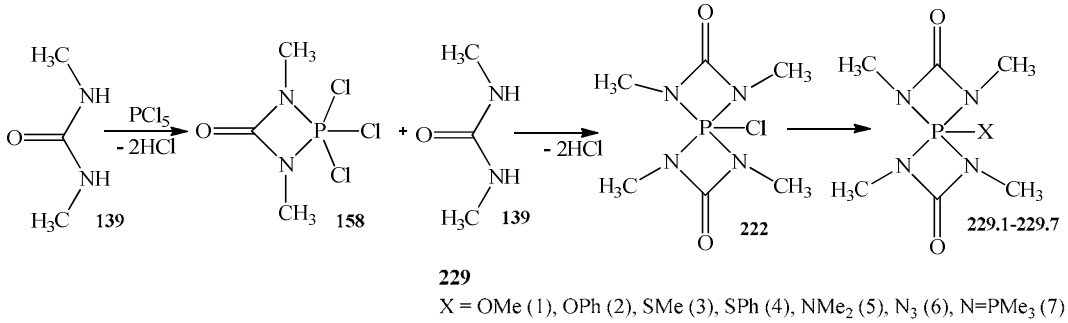
Scheme 66

Phosphaspiro[3.3]heptane-2,6-dione 228 with P-F bond was synthesized and studied with a yield of 59 % in [90] by the reaction of 91.1 with 2,2,2-trifluorodiazaphosphetidinone 163 (Scheme 67).



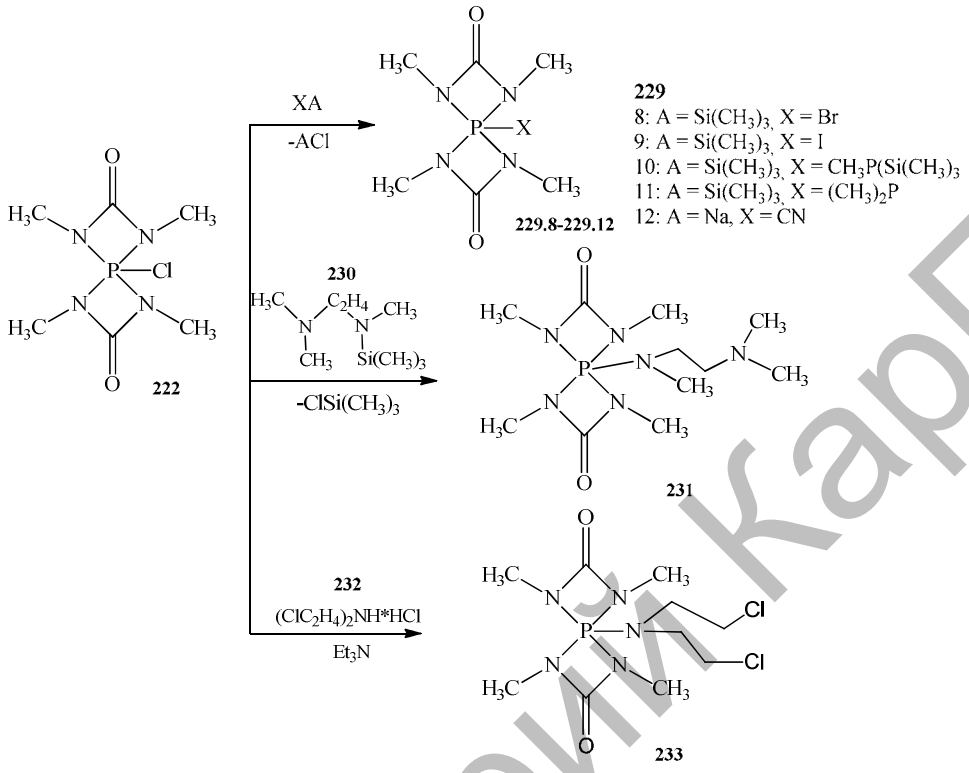
Scheme 67

Chlorophosphaspiro[3.3]heptane-2,6-dione 222 with a P–Cl bond is obtained by the interaction of symmetric dimethyl urea 139 with PCl_5 through intermediate 2,2,2-trichlorodiazaphosphetidinone 158 (Scheme 68) [90].



Scheme 68

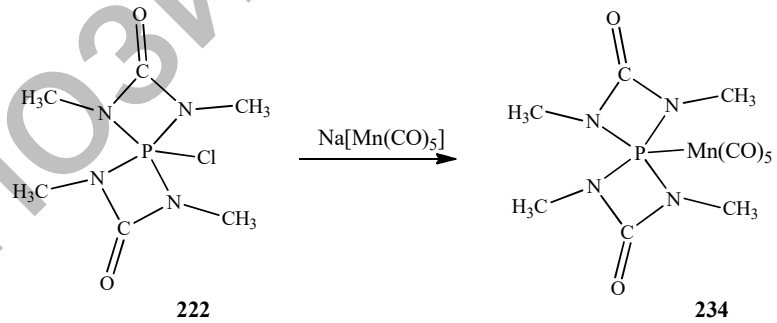
In chlorophosphaspiro[3.3]heptane-2,6-dione 222, the chlorine atom without any difficulties is subject to functionalization by various reagents with preservation of the bicyclic structure 229.1–229.12, [90, 91] (Schemes 68, 69). Similar substitution reactions were considered in [92, 93].



Scheme 69

The condensation processes of 4-chloro-1,3,5,7-tetramethyl-1,3,5,7-tetraaza-4-phosphaspiro[3.3]heptane-2,6-dione 222 with trimethyl-(trimethylsilyl)ethane-1,2-diamine 230 and bis-2-chloroethylamine 232, during which bicyclic bisureas with P–N bond 231 and 233 were obtained, respectively [92, 93].

The ability to complexation 222 was considered in [94], where it was found that the chlorine atom in an inert medium is replaced by pentacarbonylmanganese 234 (Scheme 70).

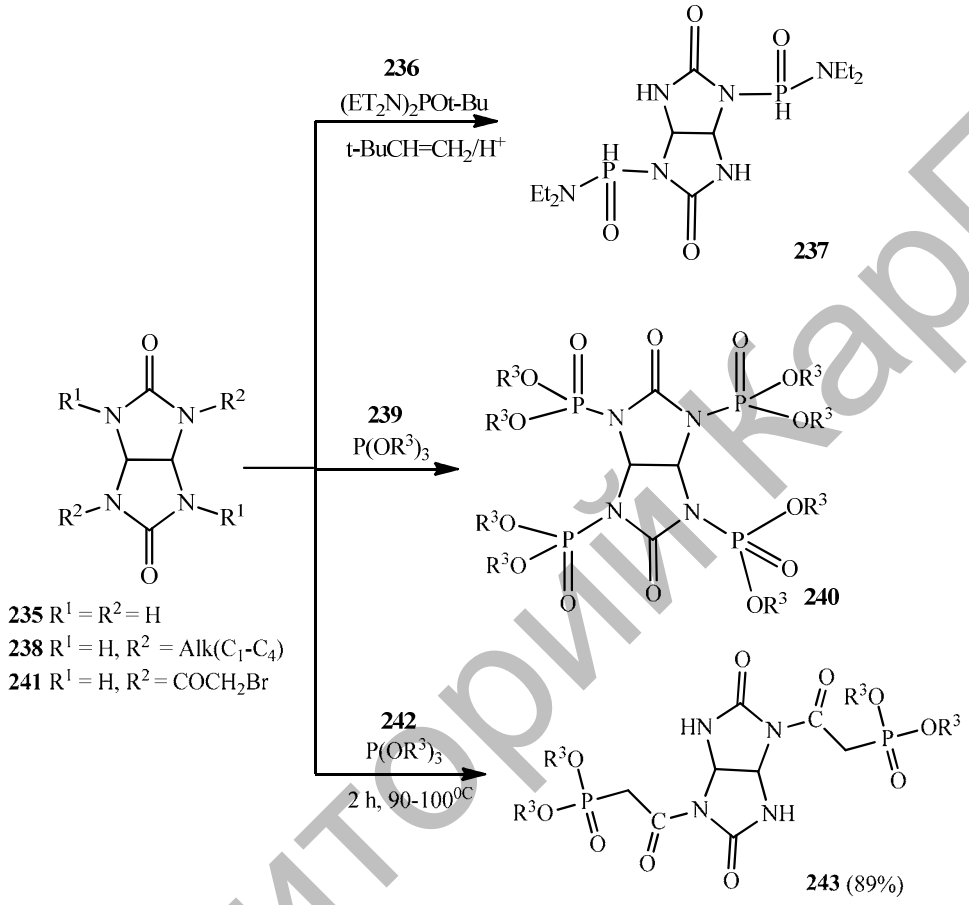


Scheme 70

3.3 Phosphorylated tetraazabicyclo[3.3.0.]octane-3,7-diones

The analysis of the available literature data has shown that the range of information on phosphorylation reactions of 2,4,6,8-tetraazabicyclo[3.3.0.]octane-3,7-dione (glycoluril) 235 has been expanding. Glycoluril 235 is product of bicyclization of urea and is its derivative, but, unlike urea, glycoluril 235 is multifunctional. Glycoluril 235 has four donor groups (–NH) and two acceptor (C=O) groups. According to chemical properties, glycoluril is a typical N-nucleophile and is easily able to enter phosphorylation reactions.

The authors [95] investigated the reaction of transamidation using glycoluril 235 and tetraethyl diamido-tert-butyl phosphite 236, which led to the formation of glycoluryl substituted diethylamido-tert-butylphosphite 237 (Scheme 71). The reaction was carried out by heating the mass of glycoluril 235 and tetraethyldiamido-tert-butylphosphite 236 in a 1:2 ratio in ethyl acetate. This ratio allows two t-butylphosphite 236 molecules to be coordinated to two amino groups (positions 2, 6). At the same time, the valence of the phosphorus atom is preserved, which causes considerable interest in this product for further research.



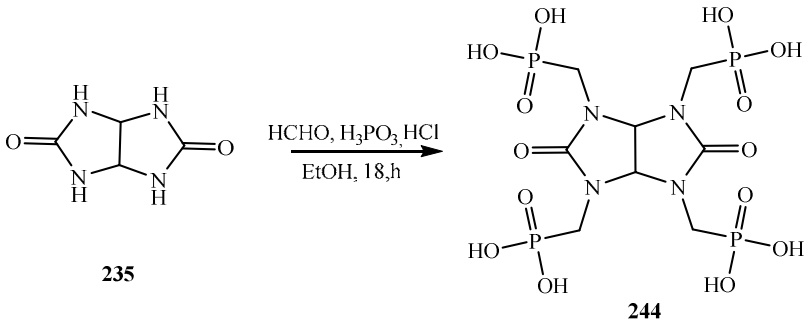
Scheme 71

In a series of Chinese patents [96–98] flame retardant substances N-phosphorylated derivatives of glycoluril 240 and methods for their preparation based on N-alkyl derivatives of glycoluril 238 (Scheme 71) were developed. These compounds are excellent nitrogen-phosphorus synergistic flame retardants.

The high nucleophilicity of the phosphorus atom is ensured by the presence of a lone electron pair on the phosphorus atom, as well as by the donor effect of alkyl groups, which facilitate the second stage of the Arbuzov's reaction — dealkylation.

The authors [99] obtained 2,6-di(1-diethylphosphonoacetyl)2,4,6,8-tetraazobicyclo[3.3.0]octane-3,7-dione 243 by phosphorylation of 2,6-di(1-bromoacetyl)-2,4,6,8-tetraazobicyclo[3.3.0]octane-3,7-dione 241 with an equimolar amount of triethyl phosphite 242. Phosphonic acids have significant biological activity compared to their esters, which causes some interest in such structures.

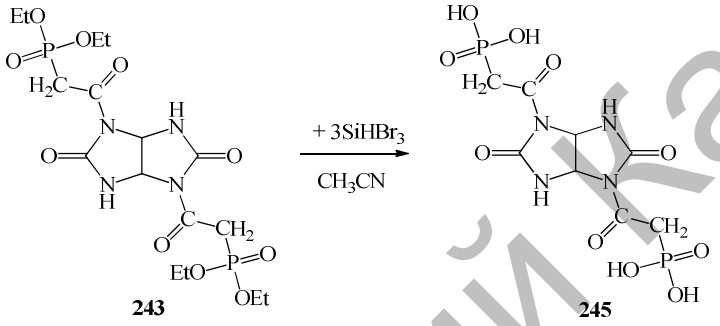
The authors [100] used glycoluryl tetrakis(methylene phosphoric acid) 244 as an effective catalyst for the synthesis of pyrazole-5,10-dione derivatives. The main advantages of using this catalyst are high yields, quick reaction and the possibility of multiple use of the catalyst. Substance 244 is synthesized by single-stage N-transalkylation of glycoluril 235 with p-formaldehyde and phosphorous acid in boiling ethyl alcohol under reflux (Scheme 72).



235 **244**

Scheme 72

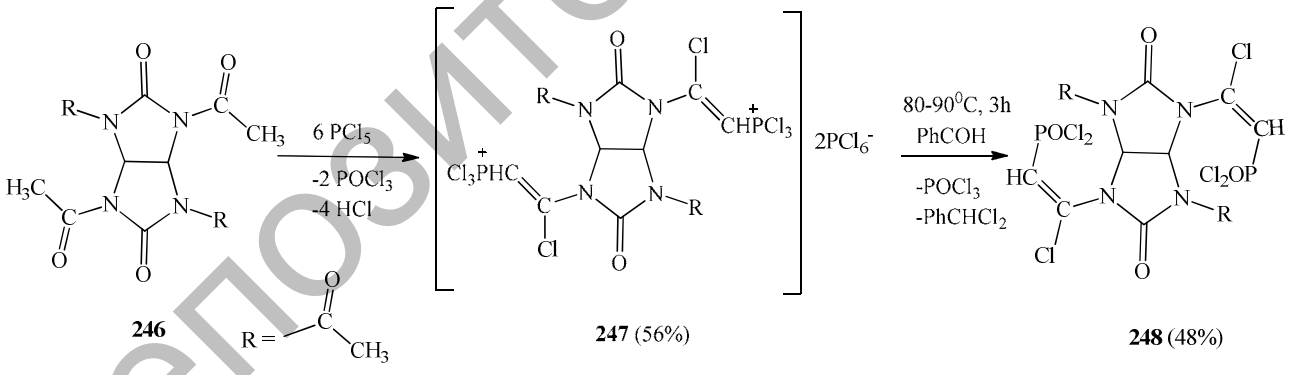
Authors [99] carried out acid hydrolysis of diphosphonate 243 with tribromosilane in acetonitrile, leading to the corresponding diphosphonic acid 245 (Scheme 73).



243 **245**

Scheme 73

Diphosphone complex of teraacetylglycoluril – 2,6-di-(4,8-diacetyl-2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione)2,6-di-(6,8-dione)-2,6-di-(chloro-ethenyltri-chlorophosphonium) 247 was obtained in [101]. It 247 is a white crystalline, unstable in air compound obtained by the phosphorylation of 2,4,6,8-tetraacetyl-2,4,6,8-tetraazabicyclo[3,3,0]octane-3,7-dione 246 with phosphorus pentachloride (Scheme 74).



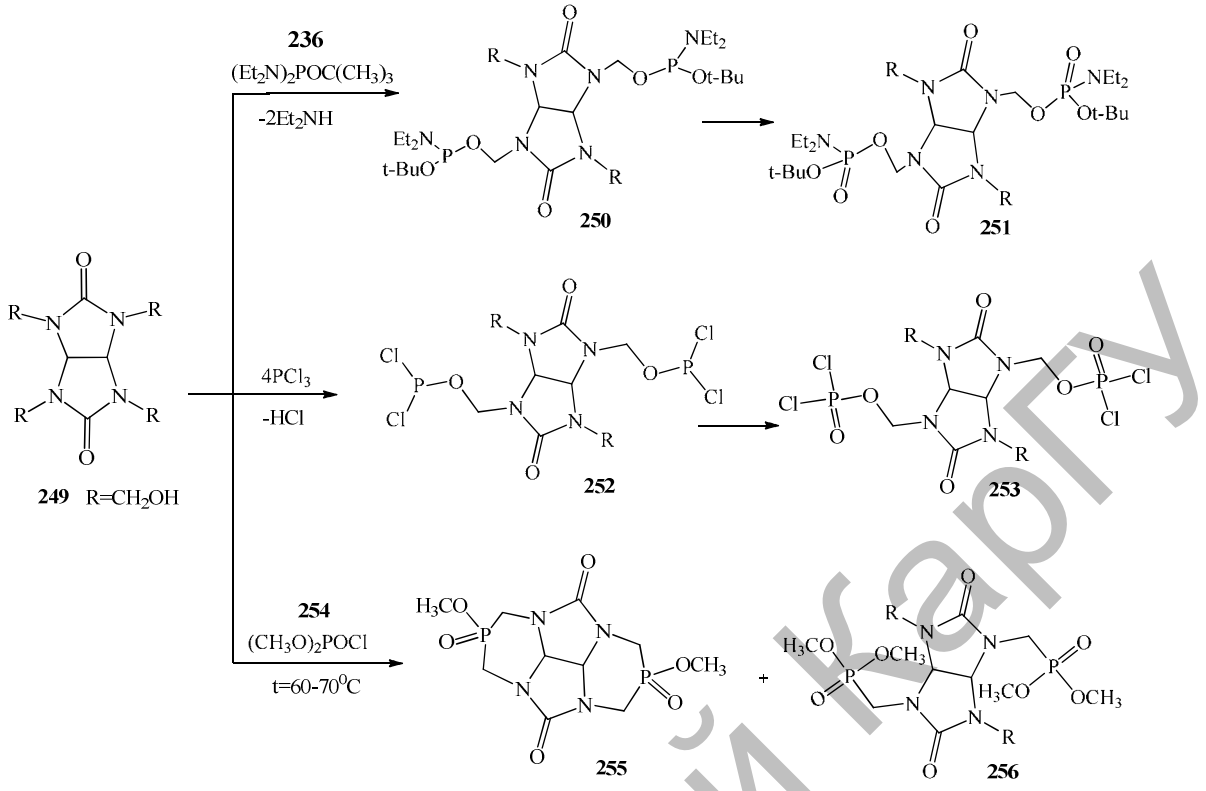
246 **247** (56%) **248** (48%)

Scheme 74

The reaction takes place when heated under argon in trichloromethane in the ratio of 1 mol 2,4,6,8-tetraacetyl-2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione 246 to 6 mol phosphorus pentachloride.

The reaction proceeds through the stage of addition of phosphorus pentachloride at the oxygen atom of the acetyl group to form complex 247, which is further decomposed by benzaldehyde to produce 248 (Scheme 74).

The phosphorylation reaction of tetra-N-methylolglycoluryltetraethyldiamido-tert-butylphosphite 236 [95] was carried out in ethyl acetate with simultaneous distillation of diethylamine. As a result, the oily product 2,6-di- (N-diethylamidomethylolphosphato)-2,4,6,8-tetraazobicyclo[3.3.0.]octane-3,7-dione 25 was isolated through the formation of intermediate product 252 (Scheme 75).



Scheme 75

When studying the reactivity of tetra-N-methylol glycoluril 249 in phosphorylation reactions, its interaction with phosphorus trichloride was carried out [95] (Scheme 75). Phosphorylation was carried out under fairly mild conditions in hexane when heated. The isolated yellow crystalline substance of 2,6-di-(N-methyl chlorophosphato)-4,8-chloromethyl-2,4,6,8-tetraazobicyclo[3.3.0.]octane-3,7-dione 253 was the product of oxidation of phosphoric fragments in compound 252 to the pentavalent state (Scheme 75).

It is known [102] that among the compounds of trivalent phosphorus, phosphorous ester amides are fairly easily exchanging the amide group under the action of alcohols, amines and phenols. This method is very convenient for obtaining amidophosphites that are difficult to access in the direct synthesis.

Reaction 249 in absolute benzene with two equivalents of dimethoxychlorophosphate 254 and pyridine as an acceptor of hydrogen chloride leads to the formation of a mixture of products 255 and 256 (Scheme 75). The reaction proceeds with a strong heat release, requiring significant cooling. The structures of the synthesized compounds 255 and 256 were proved using the data of IR, NMR spectra [95].

Summarizing the available literature data on the methods of synthesis and properties of phosphorylated bicyclic bisureas, it should be noted that the latter are represented by diphosphadionic 202–209, 212–221, diphosphaspirooctandionic 169, 222, 224, 225, 227–229, 231, 233,234 and phosphorylated tetraazabicyclooctandione structures 237, 240, 243–245, 247, 248, 250–253, 255, 256. Structural differences of the above phosphorylated compounds lie in the fact that diphosphadiones 202–209, 212–221 have a nodular bridge link that can contain three and/or pentavalent phosphorus.

Diphospaspiroooctanediones 169, 222, 224, 225, 227–229, 231, 233, 234 contain a central (nodal) pentavalent phosphorus atom that conjugates two cycles. Phosphorylated tetraazabicyclooctandiones 237, 240, 243–245, 247, 248, 250–253, 255, 256 are principally distinguished by the fact that they do not contain an endocyclic phosphorus atom. A special case is represented by bicyclic bisureas of the glycoluril series, which have phosphorylated substituents only in side chains, which makes them attractive for further transformations.

This work systemizes knowledge of reactions of ureas and their derivatives with phosphorus containing reagents by compiling overview information. Since there is currently no information available in literature summarizing the methods of synthesis and studies of phosphorus derivatives of carbamide containing compounds, this work can serve as a tool for a better understanding of the tendency of the development of synthetic works in the field of obtaining of in the field of phosphaze compounds.

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Фосфорланған карбамидқұрамды ациклді және гетероциклді қосылыстарды синтездеу әдістері

Мақалада алғаш рет мочевина және оның гетероциклді туындыларының фосфоркұрамды реагенттермен реакциясын зерттеудің қазіргі күйін жүйелеуге талпыныс жасалды. Қолданылатын субстраттар мен реагенттердің айтарлықтай айырмашылығына байланысты, шолуда фосфирленген азотқұрамды қосылыстарды алу әдістері оның құрылымына сәйкес түзілуіне қарай үш бағыт бойынша жіктелді: ациклді, моноциклді және бициклді мочевиналардың синтезі. Мысалы, жұмыста N-фосфоизоцианаттардың құрылымы әртүрлі алифатты және ароматты аминдермен реакциясы нәтижесінде N-фосфорленген мочевинаны синтездеп алудың әдістері қарастырылған, осы қосылыстарды алудың балама сирек қолданылатын әдістері келтірілген. Фосфирленген моноциклді карбамидқұрамды қосылыстарың синтездеп

алудың белгілі әдістерін талдау нәтижесінде бесмүшелі фосфазациклдер имидазолидинді құрылымы түрінде келтірілген, ал тетрацикліді фосфазациклдер диазафосфетидинондар құрылымды, алтымүшелі фосфазациклдер — диазофосфориндер және триазафосфоринандионондар түрінде болатындығы көрсетілген. Синтезделген және зерттелінген фосфорланған бициклді бисмочевиналар дифосфадионды, дифосфаспирооктандионды және фосфорланған тетраазабициклооктандионды құрылымдарда көрсетілген. Фосфорланған мочевина химия мен технологияның көптеген салаларында қолдануда қызығушылық туғызады. Фосфорланған мочевиналарды синтездеп алудың әдістері бойынша зерттеу жұмыстарының нәтижелерін жүйелеу нәтижесінде зерттеуді әрі қарай дамыту жаңа тиімділігі жоғары дәрілік заттарды алудың әдістерін іздестіруге мүмкіндік береді.

Кілт сөздер: мочевина, фосфорлану, гетероциклді қосылыстар, N-фосфоизоцианаттар, имидазолидиндер, диазафосфетидинондер, диазофосфориндер, триазафосфоринандионондар, дифосфадиондар, дифосфаспирооктандиондар, фосфорланған тетраазабициклооктандиондар, гликолурил.

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Методы синтеза фосфорилированных карбамидсодержащих ациклических и гетероциклических соединений

В статье впервые предпринята попытка систематизации современного состояния знаний в области исследования реакций мочевин и их гетероциклических производных с фосфорсодержащими реагентами. Ввиду существенных различий используемых субстратов и реагентов, в обзоре методы получения фосфорилированных азотсодержащих соединений согласно их конечной структуре сгруппированы по трем направлениям их образования — синтез ациклических, моноциклических и бициклических мочевин. Так, в работе рассмотрены методы получения ациклических N-фосфорилированных мочевин реакциями соответствующих N-фосфоизоцианатов с алифатическими и ароматическими аминами различного строения, а также приведены редко применяемые альтернативные методы синтеза такого рода соединений. Анализ известных методов синтеза фосфорилированных моноциклических карбамидсодержащих соединений свидетельствует о том, что пятичленные фосфазациклы в большинстве представлены имидазолидиновыми структурами, тогда как тетрациклические фосфазациклы — диазафосфетидинонами, а шестичленные фосфазациклы — диазофосфоринами и триазафосфоринандиононами. Синтезированные и изученные фосфорилированные бициклические бисмочевины представлены дифосфадионовыми, дифосфаспирооктандионовыми и фосфорилированными тетраазабициклооктандионовыми структурами. Самостоятельный интерес фосфорилированные мочевины представляют для развития перспектив их практического применения в различных областях химии и технологий. Сделан вывод о том, что на основании проведенной систематизации результатов экспериментальных исследований по методам синтеза фосфорилированных мочевин можно ожидать, что их развитие позволит найти пути получения новых высокоэффективных лекарственных средств и синтонов их получения.

Ключевые слова: мочевина, фосфорилирование, гетероциклические соединения, N-фосфоизоцианаты, имидазолидины, диазафосфетидиноны, диазофосфорины, триазафосфоринандиононы, дифосфадионы, дифосфаспирооктандионы, фосфорилированные тетраазабициклооктандионы, гликолурил.

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