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Trichloropyruvate *N*-Acylimines. Reactions with Phosphorus Nucleophiles

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Abstract—Reactions of *N*-aroyltrichloroethaneimines $CCl_3C(R)=NCOAr$ (**II**, R = COOMe, CN) with phosphorus nucleophiles were studied. The reaction of imines **II** with *o*-phenylenediethylamidophosphite proceeded as [4+1]-cycloaddition leading to formation of stable spirocyclic phosphoranes. The structure of one of them was proved by the XRD analysis. The reaction of imine **II** with acyclic P(III) derivatives [Ph_3P, Ph_2POEt, $(PhO)_3P$] also includes the formation of labile monocyclic phosphoranes which eliminate phosphine oxide and undergo chlorotropic transfer leading to trichloroazadienes $CCl_2=C(R)N=C(Cl)Ar$. The reaction of imines **II** with $(EtO)_2POH$ in the presence of triethylamine leads to the formation of $(EtO)_2P(O)Cl$ and the corresponding dichlorovinylamides $CCl_2=C(R)NHCOAr$.

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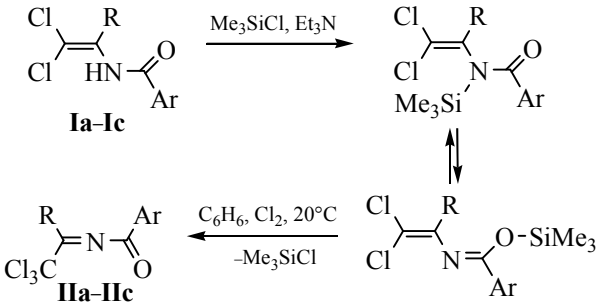
N-Acylamines are valuable highly reactive building blocks in the synthesis of various nitrogen-containing compounds [1–4]. Activated imines with the carboxyl group at the imine carbon atom are of special interest because their functionalization leads to derivatives of α-amino acids exhibiting high biological activity. For example, trifluoropyruvate *N*-acylamines easily react with nucleophilic and dipolar reagents to form biologically important derivatives of trifluoroalanine [3, 5–7]. At the same time imines of trichloropyruvates until recently were not practically studied because preparative methods of their synthesis were lacking. We have developed lately a convenient method for the preparation of trichlotopyruvate *N*-acylimines from dichlorovinylamides **I** (Scheme 1) [8]. It was shown that these substances easily react with S-,O-,N-, and C-nucleophiles to form functional derivatives of α-amino acids containing trichloroalanine fragment. It turned out that this method was sufficiently universal and was suitable for the synthesis of previously unknown nitriles of acyliminotrichloropropanoic acids **II** (R = C≡N). In the work the synthesis is described of the first representative of such compounds **IIc** and the reactions of phosphorus nucleophiles with *N*-aroyl-imines containing methoxycarbonyl (**IIa, IIb**) or nitrile group at the imine carbon atom.

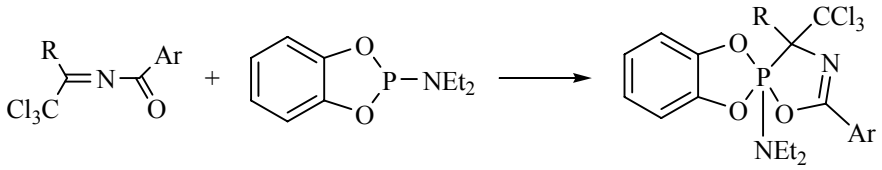
Scheme 1.



R = COOMe, Ar = Ph (**a**), 4-MeC_6H_4 (**b**) [8]; R = CN, Ar = Ph (**c**).

Analysis of published data shows the variety of pathways taken by the reaction of *N*-acyl-α-haloalkane-imines with nucleophilic phosphorus derivatives [9]. In particular, haloalkane acylimines can react with the participation of the C=N bond, of haloalkyl fragment, or heterodiene system C=N–C=O to give the products of C- and/or N-phosphorylation which in their turn often undergo further transformations [9]. The direction of these reactions is very sensitive to the nature of substituents at the azomethine bond, the nature of phosphorus reagent, and halogen in the haloalkyl fragment. For iminocarboxylates **IIa, IIb** and

Scheme 2.



IIa–IIc **III** **IVa–IVc**

R = COOMe, Ar = Ph (**a**), 4-MeC_6H_4 (**b**); R = CN, Ar = Ph (**c**).

nitrile **IIc** containing the system of heterodiene bonds all the above-described directions are possible and the result of the reaction with trivalent phosphorus compounds is not evident.

It was found that the direction of the reactions of compounds **IIa–IIc** with phosphorus nucleophiles significantly depends on the nature of the phosphorus reagent. With cyclic amidophosphite **III** they react according to the type of [4+1] cycloaddition leading to the formation of stable pentacoordinate phosphorus compounds **IVa–IVc** (Scheme 2).

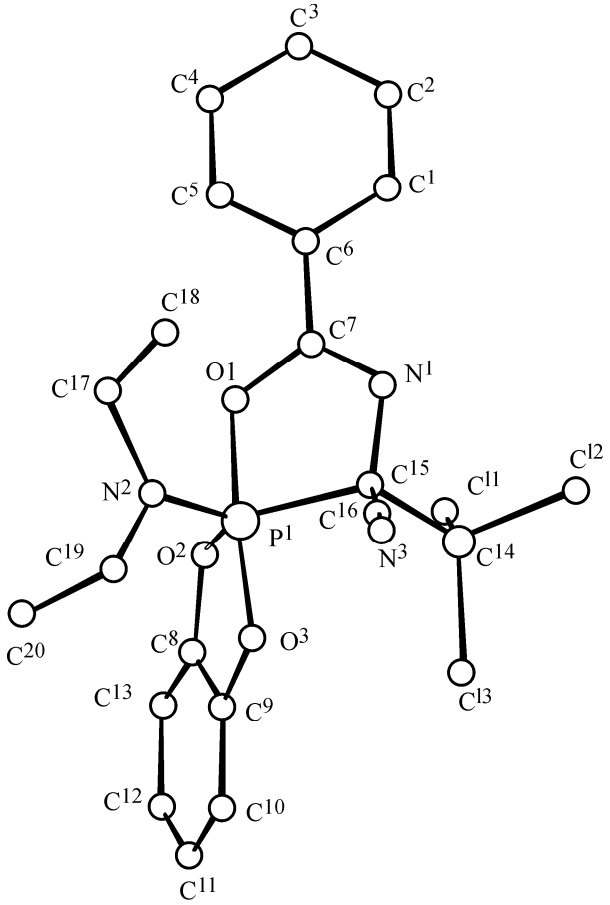
Compounds **IV** are the representatives of the new type of spirophosphoranes containing the fragments of α-aminocarboxylic and α-aminophosphonic acids in the oxazaphospholine cycle. They contain two chiral centers and may exist as various diastereomers. It was found that stereoselectivity of the process shown in Scheme 2 depends on the nature of substituents in the imine. Esters **IIa, IIb** in the reaction with phosphite **III** form a mixture of two diastereomers **IVa, IVb** (δ_P^A –21.3 and –21.0 ppm, δ_P^B –19.7 and –19.5 respectively, A/B ~ 1.3 : 1 and 1.1 : 1 respectively). At the same time nitrile **IIc** under the same conditions gives only one diastereomer **IVc** (δ_P –21.7 ppm). Hence, stereoselectivity of the reaction correlates with electron-acceptor properties of substituents in imines **II**: **IIc** > **IIa** > **IIb**. Note that in the initial step of the reaction of compounds **IIa–IIc** with phosphite **III** the appearance of a weak (10–15%) signals of phosphorus nuclei (δ_P –25.5, –25.3 and –25.0 ppm respectively) was observed in ^{31}P NMR spectra. Within 24 h they disappeared. These signals can also be attributed to diastereomeric forms of phosphoranes **IV**. Stereomers **A** and **B** of spirophosphoranes **IVa, IVb** are conformationally stable and under usual conditions do not transform into one another. At the same time after one washing of diastereomer mixture of compounds **IVa** with ether solid phase is enriched with the isomer **B** (**A/B** = 1:6), and the filtrate with isomer **A** (**A/B** = 7:1).

Structure of spirophosphorane **IVc** was unambiguously established by XRD analysis. It is known that phosphoranes are suggested as transition states in many reactions, in particular, of the enzymatic transfer of the phosphoryl group important for biochemical processes [10]. Only several examples of structural data for spirophosphoranes were found in the literature [11, 12, 13], and for bicyclic phosphoranes containing P-C bond in spirocycle no data were known. Due to that the investigation of specific features of spatial arrangement of spirocyclic phosporane **IV** presents doubtless interest. It is also important that the isolated stereoisomer **IVc** according to ^{31}P NMR data is analogous to the preferably formed diastereomer **A** of compounds **IVa, IVb**. Compound **IVc** crystallizes in centrosymmetric space group. General view of molecule is presented in the figure. Main bond lengths and bond angles are listed in the table.

It is established that phosphorus atom in the structure of molecule **IVc** has the distorted trigonal bipyramide coordination with the atoms O^1 and O^3 in the axial and O^2, N^2, and C^{15} atoms in the equatorial positions. The distortion of trigonal bipyramide is revealed in the decrease in the angle between the axial bonds to 171.16(9)°, and also in the non-equivalence of angles in the equatorial plane [angles $O^2P^1N^2$, $O^2P^1C^{15}$, and $N^2P^1C^{15}$ are 121.36(9)°, 124.19(9)°, and 113.98(0)° respectively]. Phosphorus atom is located in the equatorial plane [sum of equatorial angles is 259.5(2)°]. N^2 nitrogen atom has the planar trigonal coordination [sum of bond angles id 359.9(5)°].

Five-membered $P^1O^1C^7N^1C^{15}$ cycle has the *envelope* conformation. $C^1C^6N^1C^{15}$ atoms are coplanar (root-mean-square deviation of atoms from the plane of heterocycle is 0.001 Å), and the point of envelope $C^{15}P^1O^1$ forms with the above-mentioned plane an angle equal to 11.69°.

In the ^{13}C NMR spectrum spatial nonequivalence of equatorial (O^2) and axial (O^3) oxygen atoms of dioxaphospholane ring is revealed in the magnetic nonequivalence of C^8, C^9, C^{10}, and C^{13}, C^{11} and C^{12} atoms of dioxyphenylene ring, and also in the



General view of molecule of compound **IVc** (hydrogen atoms are not shown).

significant difference in coupling constants (J_{CP}) of these pairs of carbon nuclei with phosphorus: δ_C^A 147.2 s, δ_C^B 142.8 d, $^2J_{CP}$ 5.8 Hz (C^8, C^9); δ_C^A 112.24 d, $^2J_{CP}$ 16.8 Hz, δ_C^B 111.8 d, $^3J_{CP}$ 9 Hz (C^{10}, C^{13}); δ_C^A 122.4 s, δ_C^B 124.4 s (C^{11}, C^{12}).

By the method of competing reactions we have evaluated the relative reactivity of nitrile **IIc** and esters **IIa, IIb** with respect to amidophosphite **III**. It was found that after introduction of nitrile group in substrates **IIa, IIb** instead of methoxycarbonyl one the reaction with amidophosphite significantly accelerates ($k_{IIc}/k_{IIa,\ IIb}$ ~ 10). Hence, the increase in electron-acceptor properties of substituent R at the imine carbon atom (σ_P^{COOMe} 0.39, σ_P^{CN} 0.66) leads to the increase in the rate of the process. The established effect of substituents agrees with the fact that cycloaddition shown in Scheme 2 proceeds stepwise. Nucleophilic attack of the imine carbon atom with phosphite is the rate-limiting stage, and the bipolar ion formed is stabilized by the intramolecular cyclization. Hence, the introduction of nitrile group instead of methoxycarbonyl one increases the rate of the reaction as well as its stereoselectivity.

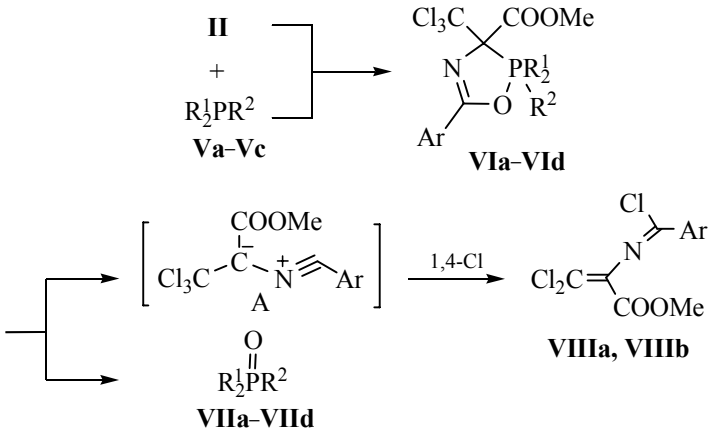
Reactions with acyclic phosphites and triphenylphosphine. The reaction of heterodienes with the acyclic derivatives of trivalent phosphorus **Va-Vc** also proceeds through the formation of monocyclic phosphoranes **VI**, the unstable products of [4+1] cycloaddition (Scheme 3). Even at room temperature they undergo transformations including the cleavage of oxazaphospholine cycle.

The rate of the formation and the stability of phosphoranes **VI** is determined by the nature of phosphorus reagent. Thus, the reaction with triphenylphosphine **Va** proceeds easily and selectively at room temperature in benzene, but phosphorane **VIa** (δ_P –44.8 ppm) quickly eliminates phosphine oxide **VIIa.** Nitrile ylide **A** generated in this process is stabilized by 1,4-chlorotropic migration and converts in imidoyl chloride **VIIIa**. Fifteen minutes after the beginning of the reaction (benzene, 15°C) the ratio of compounds **VIIa**/**VIa** is 100:4, and after 30 min according to ^{1}H and ^{31}P NMR data the quantitative formation of triphenylphospine oxide **VIIa** and imidoyl chloride **VIIIa** takes place. The reaction with diphenylphos-phinite **Vb** proceeds analogously. At the same time the weak

Main bond lengths (*d*, Å) and bond angles (ω, deg) in the molecule of compound **IVc**

Bond	*d*	Angle	ω
Cl^1–C^{14}	1.758(2)	$O^1P^1O^2$	83.91(7)
Cl^2–C^{14}	1.765(2)	$O^1P^1O^3$	171.16(8)
Cl^3–C^{14}	1.775(2)	$O^1P^1N^2$	93.95(9)
P^1–O^1	1.712(1)	$O^1P^1C^{15}$	85.81(8)
P^1–O^2	1.646(2)	$O^2P^1O^3$	90.99(8)
P^1–O^3	1.684(2)	$O^2P^1N^2$	121.36(9)
P^1–N^2	1.633(2)	$O^2P^1C^{15}$	124.20(9)
P^1–C^{15}	1.929(2)	$O^3P^1N^2$	94.87(9)
O^1–C^7	1.341(2)	$O^3P^1C^{15}$	91.14(9)
O^2–C^8	1.379(2)	$N^2P^1C^{15}$	114.0(1)
O^3–C^9	1.369(3)	$P^1O^1C^7$	113.8(1)
N^1–C^7	1.279(3)	$P^1O^2C^8$	113.4(1)
N^1–C^{15}	1.452(3)	$P^1O^3C^9$	112.5(1)
N^2–C^{17}	1.488(3)	$C^7N^1C^{15}$	110.2(2)
N^2–C^{19}	1.483(3)	$C^1C^6C^7$	119.7(2)
N^3–C^{16}	1.136(3)	$O^1C^7N^1$	121.1(2)
C^{14}–C^{15}	1.558(3)	$O^1C^7C^6$	115.4(2)
C^{15}–C^{16}	1.480(3)	$N^1C^7C^6$	123.4(2)
C^{17}–C^{18}	1.519(3)	$O^2C^8C^9$	111.3(2)
C^{19}–C^{20}	1.519(4)	$P^1C^{15}N^1$	107.3(1)

Scheme 3.



V, VII: $R^1 = R^2 =$ Ph (**a**); $R^1 =$ Ph, $R^2 =$ EtO (**b**); $R^1 = R^2 =$ PhO (**c**); **VI**: $R^1 = R^2 =$ Ph, Ar = Ph (**a**), 4-MeC_6H_4 (**b**); $R^1 =$ Ph, $R^2 =$ EtO, Ar = 4-MeC_6H_4 (**c**); $R^1 = R^2 =$ PhO, Ar = 4-MeC_6H_4 (**d**); **VIII**: Ar = Ph (**a**), 4-MeC_6H_4 (**b**).

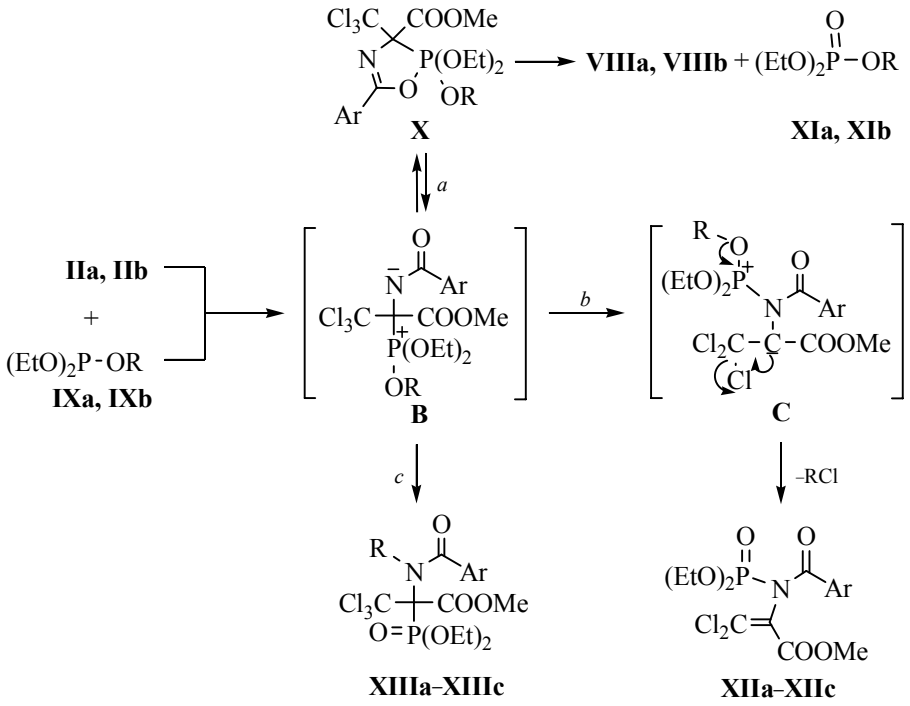
nucleophile triphenyl phosphite reacts significantly slower. A day after mixing the reagents in benzene at 15°C in ^{31}P NMR spectrum of reaction mixture together with the signals of starting phosphite **Vc** the signals of phosphorane **VId** (δ_P –45.7 ppm) and triphenyl phosphate **VIIc** (δ_P –17.3 ppm) are observed, **VIIc**/**VId** ratio being 2:1. The reaction completes only in 5 days, and a set of by-products is accumulated in the reaction mixture. From the preparative point of view the reaction with triphenylphosphine is preferred for the conversion of imines **II** in azadienes **VIII**.

While using trialkyl or silyl phosphites new pathways appear in the reaction. They are related to the possible dealkylation of quasiphosphonium or phosphorane intermediates. It is established that the reaction of imines **II** with phosphites **IXa, IXb** proceeds non-selectively with the formation of products of N- (**XII**) as well as of C-phosphorylation (**XIII)**, and also of phosphates **XI**. The obtained results can be rationalized within the frames of Scheme 4.

The attack of phosphite on the most electrophilic imine carbon atom of compounds **II** and the subsequent intramolecular cyclization of the intermediate bipolar ion **B** (pathway *a*) leads to phosphoranes **X** which transform in imidoyl chlorides **VIIIa, IIb** analogously to Scheme 3. C,N-Migration of phosphonium center in intermediate **B** (compare with [9]) and the subsequent stabilization of carbanion **C** by the elimination of ethyl or trimethylsilyl chloride leads to the product of the aza-Perkow reaction **XII** (pathway *b*). The stabilization of bipolar ion **C** may also be achieved by O,N-migration of ethyl or trimethylsilyl group (pathway *c*) with the formation of phosphonates **XIII**. According to NMR spectral data the ratio of the directions *a*, *b*, and *c* is 1:0.76:0.1 (R = Et) and 1:1:0.5 (R=Me_3Si) respectively. The increase in the yield of C-phosphorylated product **XIIIc** in the reaction with (diethyl)trimethylsilyl phosphite is due to the high migration ability of trimethylsilyl group favoring the transformation of the intermediate **B** in the product **XIIIc** (Scheme 4). Spectral monitoring of dynamics of this process confirms the proceeding of the reaction through the intermediate formation of phosphoranes **X**. For example, 15 min after the beginning of the reaction of imine **IIa** with triethyl phosphite (benzene, 15°C) signals of phosphorane **X** (R = Et, Ar = Ph) (–35.7 ppm), of phosphorylated dichlorovinylamide **XIIa** (–1.8 ppm), of triethyl phosphate **XIa** (0.6 ppm), and of starting phosphite **IXa** (139.3 ppm) were observed in ^{31}P NMR spectrum. The ratio of these signals was **Xa**:**XIIa**:**XIa**:**IXa** ~ 1.3:1:0.9:0.3. After 12 h the signals of triethyl phosphite and phosphorane disappear and a weak signal of phosphonate **XIIIa** (9.4 ppm) appears, the ratio **XIIa**:**XIa**:**XIIIa** being 1:0.8:0.1. The attribution of signals of compounds **XII,XIII** in ^{31}P NMR spectra was carried out on the basis of comparison with the reported data [14, 15].

Reaction with hydrophosphoryl compounds. We showed recently that N-, O-, or S-centrated X–H nucleophiles even in the absence of base easily added to the C=N bond of iminocarboxylates **IIa, IIb** with the formation of functionalized derivatives of trichloroalanine [1]. With diethyl hydrogen phosphite, the P-centrated nucleophile, the reaction proceeds

Scheme 4.



IX, XI: R = Et (**a**), Me_3Si (**b**); **XII, XIII**: R = Et, Ar = Ph (**a**), 4-MeC_6H_4 (**b**); R = Me_3Si, Ar = 4-MeC_6H_4 (**c**).

more complex. In this case initially formed products of addition to the C=N bond, phosphonates **XIV** (δ_P 9.6–11.4 ppm), were found only spectroscopically (compare with [9, 16]). Even at room temperature they undergo ambiguous transformations including the transfer of phosphoryl group and the formation of N- and O-phosphorylated products [9, 14–16] (δ_P from –5.4 to –5.9 ppm and from –8.4 to –8.9 ppm) and the destruction of the latter (δ_P from –0.3 to –1.1 ppm). Note also that the reaction of diethyl hydrogen phosphite with more reactive nitrile **IIc** proceeds even in low polar benzene. At the same time for performing the reaction with iminocarboxylate **IIb** the presence of dipolar solvent such as DMSO is necessary. In benzene in the absence of a base no reaction takes place. Hence, in the absence of bases the reaction of imine **II** with diethyl hydrogen phosphite proceeds non-selectively and cannot be used for the synthesis of the corresponding phosphonates. As is known, the catalysis with bases facilitates the nucleophilic reactions of hydrophosphoryl compounds, in particular, the Pudovik reaction. At the same time it proved that using triethylamine principally changes the pathway of the reaction of imines **IIb, IIc** with diethyl hydrogen phosphite. In this case the formation of diethyl chlorophosphate and dichlorovinylamides **Ib, Ic** takes place (Scheme 5). Such unexpected route of the reaction may be due to the elimination of diethyl chlorophosphate from the adducts or to the halophilic attack of phosphite ion on the positivated chlorine atom of trichloromethyl group of the imines **IIa–IIc**.

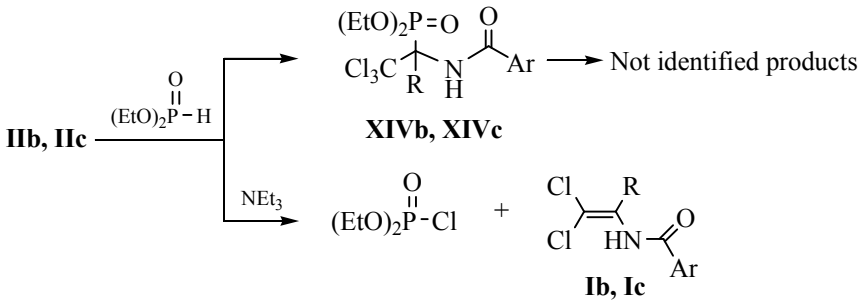
Hence, reactions of N-aroyltrichloroethaneimines **II** with nucleopilic P(III) derivatives depending on the nature of substituents at phosphorus include [4+1]-cycloaddition, addition to the C=N bond, and involving CCl_3 group in the process. They can be also accompanied by rearrangements and degradation of the products.

EXPERIMENTAL

IR spectra were registered on an UR-20 spectrometer. NMR spectra were taken on a Varian VXR-300 (^{1}H), Bruker Avance DRX-500 (^{1}H, ^{13}C), and Varian Gemini-200 (^{31}P) spectrometers with working frequencies 299.95, 500.07, 125.76, and 81.03 MHz respectively. Chemical shifts were measured with respect to internal TMS (^{1}H, ^{13}C) and external 85% H_3PO_4 (^{31}P). All the reactions were carried out in anhydrous conditions under argon.

XRD study of the single crystal of compound **IVc** was carried out on an automatic Bruker Apex II

Scheme 5.



XIVb: R = COOMe, Ar = 4-MeC_6H_4; **XIVc**: R = CN, Ar = Ph.

diffractometer at –100°C. For the evaluation of parameters of the unit cell and orientation matrix of the crystal of compound **IVb** with linear dimensions 0.47×0.47×0.61 mm 9716 reflections with $2.20 < \theta < 26.34°$ were collected. On the whole 22420 reflections were collected among which 4478 were symmetrically independent (averaging *R*-factor 0.028). Crystals of compound **IVa** are monoclinic, *a* 11.4407(2), *b* 9.9134(2), *c* 19.5542(4) Å, β = 97.602(1)°, *V* 2198.27(7) $Å^3$, *Z* = 4, d_{calc} 1.471, μ 0.517 mm^{-1}, *F*(000) 1000, space group $P2_1/n$ (no. 14). The structure was solved by the direct method and refined by the root-mean-square method in the full-matrix anisotropic approximation using the CRYSTALS software [17]. In the refinement 3364 reflections were used with $I > 3\sigma(I)$ (271 refined parameter, number of reflections per parameter 12.4). Chebyshev weight scheme was used with the coefficients –9.10, –25.9, –22.3, –15.3, –5.84. All hydrogen atoms were revealed objectively from the Fourier difference series and included in refining with the fixed heat and positional parameters. Final values of scattering factors *R* 0.0378 and R_w 0.0321, GOF 1.0694 by the reflections with $I > 3\sigma(I)$. Residual electronic density from the differential Fourier series 0.75 and –0.63e/$Å^3$. All crystallographic data were deposited in the Cambridge structured bank, CCDC 814132.

***N*-Benzoyltrichloroacetimidoylcyanide (IIc)**. To the solution of amide **Ic**, 27.4 mmol and trimethylchlorosilane, 27.4 mmol, in 120 ml of anhydrous benzene 41.1 mmol of triethylamine was added with stirring. After 2 days triethylamine hydrochloride was filtered off and washed with 50 ml of benzene. To the filtrate a solution of 100 mmol of chlorine in 30 ml of benzene was added at 5–10°C. The obtained solution was stirred at room temperature for 12 h, the solvent was evaporated in a vacuum, and the residue was crystallized from cyclohexane. Yield 87%, mp 105–110°C (from cyclohexane). IR spectrum (KBr), ν, cm^{-1}: 1650, 1697 (C=N, C=O), 2375 (C≡N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.5 d (2H, $^3J_{HH}$ 7.4 Hz), 7.73 t (1H, $^3J_{HH}$ 7.5 Hz), 7.93 d (2H, $^3J_{HH}$ 7.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 91.78 (CCl_3), 106.94 (C≡N), 129.26 (*ipso* C, Ph), 129.34, 130.00 (*o*-C, *m*-C, Ph), 135.58 (*p*-C, Ph), 139.26 (C=N), 174.56 (C=O). Found, %: C 43.60, H 1.86, Cl 39.00, N 10.15. $C_{10}H_5Cl_3N_2O$. Calculated, %: C 43.59; H 1.83, Cl 36.60; N 10.17.

2-Aryl-4-R-7,8-benzo-5-diethylamino-4-trichloromethyl-1,6,9-trioxa-3-aza-5-phosphaspiro[4.4]non-2-enes (IVa–IVc). To a solution of 27.4 mmol of imine **II** in 5 ml of anhydrous benzene 27.4 mmol of amidophosphite **III** was added with stirring. Reaction mixture was stirred for 12 h, the solvent was removed in a vacuum and the residue was washed with petroleum ether.

7,8-Benzo-5-diethylamino-4-methoxycarbonyl-4-trichloromethyl-2-phenyl-3-aza-1,6,9-trioxa-5-phosphaspiro[4.4]-non-2-ene (IVa). Yield 93%. IR spectrum (KBr pellet), ν, cm^{-1}: 1640 (C=N), 1735 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: diastereomer **A**: 1.04 t (3H, MeC, $^3J_{HH}$ 6.0 Hz), 1.42 t (3H, Me_3C, $^3J_{HH}$ 6.9 Hz), 2.88–3.02 m (2H, NCH_2), 3.05 s (3H, MeO), 3.64–3.85 m (2H, NCH_2), 6.8–7.0 m (4H, OC_6H_4), 7.52 t (2H, 3,5 H_{Ph}, $^3J_{HH}$ 7.4 Hz), 7.61 t (1H, 4-H_{Ph}, $^3J_{HH}$ 7.4 Hz), 8.22 d (2H, 2,6-H_{Ph}, $^3J_{HH}$ 7.2 Hz); diastereomer **B**: 0.93 br. (3H, MeC), 1.13 br. (3H, MeC), 2.7–3.0 m (2H, NCH_3), 3.1-3.3 m (2H, NCH_2), 3.91 s (3H, MeO), 6.9–7.1 m (4H, OC_6H_4), 7.50 t (2H, 3,5-H_{Ph}, $^3J_{HH}$ 7.4 Hz), 7.60 t (1H, 4-H_{Ph}, $^3J_{HH}$ 7.4 Hz), 8.22 d (2H, 2,6-H_{Ph}, $^3J_{HH}$ 7.2 Hz). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: –21.3 (**A**), –19.7 (**B**). Found, %: C 48.49, H 4.29, Cl 20.35, N 5.35. $C_{21}H_{22}Cl_3N_2O_4P$. Calculated, %: C 48.53, H 4.27, Cl 20.46, N 5.39.

7,8-Benzo-5-diethylamino-4-methoxycarbonyl-2-(4-tolyl)-4-trichloromethyl-3-aza-1,6,9-trioxa-5-phos-

phaspiro[4.4]-non-2-ene (IVb). Yield 88%. IR spectrum (KBr pellet), ν, cm^{-1}: 1630 (C=N), 1745 (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: diastereomer **A**: 1.03 t (3H, *Me*CH_2, $^3J_{HH}$ 6.9 Hz), 1.42 t (3H, *Me*CH_2, $^3J_{HH}$ 6.9 Hz), 2.43 s (3H, MeAr), 2.88–3.02 m (2H, NCH_2), 3.03 s (3H, MeO), 3.65–3.85 m (2H, NCH_2), 6.82–7.02 m (4H, OC_6H_4), 7.30 d (2H, H_{Tol}, $^3J_{HH}$ 7.4 Hz), 8.08 d (2H, H_{Tol}, $^3J_{HH}$ 7.4 Hz); diastereomer **B**: 0.92 br. (3H, *Me*CH_2), 1.13 br. (3H, *Me*CH_2), 2.43 s (3H, MeAr), 2.7–3.0 m (2H, NCH_2), 3.1–3.3 m (2H, NCH_2), 3.90 s (3H, MeO), 6.83–7.03 m (4H, OC_6H_4), 7.30 d (2H, H_{Tol}, $^3J_{HH}$ 7.4 Hz), 8.08 d (2H, H_{Tol}, $^3J_{HH}$ 7.4 Hz). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: –21.0 (**A**), –19.5 (**B**). Found, %: C 49.61; H 4.52; Cl 19.85; N 5.21. $C_{22}H_{24}Cl_3N_2O_5P$. Calculated, %: C 49.50; H 4.52; C 19.85; N 5.21.

7,8-Benzo-5-diethylamino-4-trichloromethyl-2-phenyl-4-cyano-3-aza-1,6,9-trioxa-5-phosphaspiro [4.4]-non-2-ene (IVc). Yield 87%, colorless crystals, mp 149–150°C (CH_2Cl_2-petroleum ether). IR spectrum (KBr pellet), ν, cm^{-1}: 1620 (C=N), 2380 (C≡N). ^1H NMR spectrum (C_6D_6), δ, ppm: 1.08 t (6H, Me, $^3J_{HH}$ 7 Hz), 2.8–3.0 m (2H, NCH_2), 3.3–3.7 m (2H, NCH_2), 6.8–6.9 m (1H, OC_6H_4), 6.96 d (2H, OC_6H_4, *J* 4.5 Hz), 7.13 d (1H, OC_6H_4, *J* 7.9 Hz), 7.33 t (2H, 3,5-H_{Ph}, $^3J_{HH}$ ~7.5 Hz), 7.39 t (1H, 4-H_{Ph}, $^3J_{HH}$ 7.3 Hz), 8.50 d (2H, 2,6-H_{Ph}, $^3J_{HH}$ 7.4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (numbering of C atoms see in the figure): 15.93 (CH_3), 46.23 d ($^2J_{CP}$ 3.5 Hz, CH_2), 79.50 d ($^1J_{CP}$ 151 Hz, CP), 99.55 d ($^2J_{CP}$ 6.8 Hz, CCl_3), 111.75 d ($^3J_{CP}$ 9 Hz) and 112.24 d ($^3J_{CP}$ 16.8 Hz) (C^{10}, C^{13}), 116.84 d ($^2J_{CP}$ 1 Hz, C≡N), 122.43 and 124.39 (C^{11}, C^{12}), 129.30 d ($^3J_{CP}$ 1.5 Hz, C^6), 129.5 and 129.5 (C^1, C^5, and C^2, C^4), 133.89 (C^3), 142.77 d, ($^2J_{CP}$ 5.8 Hz) and 147.20 s (C^9 and C^8), 165.66 d ($^2J_{CP}$ 26.9 Hz, C≡N). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: –21.7. Found, %: 48.39, H 3.40, Cl 22.57, N 8.95. $C_{19}H_{16}Cl_3N_3O_3P$. Calculated, %: C 48.38, H 3.42, Cl 22.55, N 8.91.

Azadienes (VIII). To a solution of 0.5 mmol of imine **II** in 3 ml of diethyl ether 0.5 mmol of triphenylphosphine was added at 5–10°C. After 2 h the precipitate of triphenylphosphine oxide was filtered off, the residue was evaporated and extracted with petroleum ether.

3-Methoxycarbonyl-1,4,4-trichloro-1-phenyl-2-aza-1,3-diene (VIIIa) [18]. Yield 65%. IR spectrum, ν, cm^{-1}: 1648 (C=N), 1735 (C=O). Found, %: Cl 35.86. $C_{11}H_8Cl_3NO_2$. Calculated, %: Cl 36.36.

3-Methoxycarbonyl-1-(4-tolyl)-1,4,4-trichloro-2-aza-1,3-diene (VIIIb). Yield 63%. IR spectrum, ν, cm^{-1}: 1648 (C=N), 1736 (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.43 s (3H, MeC), 3.82 s (3H, OMe), 7.27 d (2H, Ar, $^3J_{HH}$ 7.4 Hz), 8.02 d (2H, Ar, $^3J_{HH}$ 7.4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.60 (MeC), 52.87 (MeO), 122.25 (CCl_2), 129.35, 129.72 (C^2,C^3, Ar), 131.58 (=C–N), 135.03 (C^1, Ar), 144.03 (C^4, Ar), 150.09 (C=N), 161.03 (C=O). Found, %: C 47.24, H 3.12, Cl 34.07, N 4.10. $C_{12}H_{10}Cl_3NO_2$. Calculated, %: C 47.01, H 3.29, Cl 34.69, N 4.57.

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