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Sigmatropic Isomerizations in Azaallyl Systems: XXI.[1] Alkanimidoylphosphonates and Their Prototropic and Phosphorotropic Isomers

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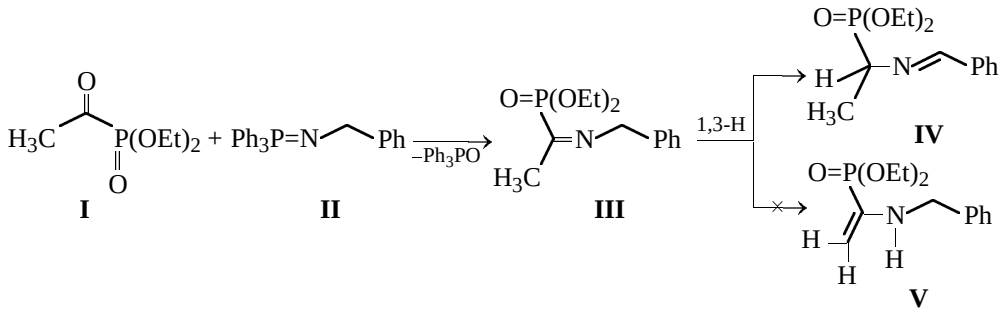
Abstract — Synthetic procedures for alkanimidoylphosphoryl derivatives with α-hydrogen atoms in the *N*-alkyl radical are developed. Data on the effect of substituents at the carbon and phosphorus atoms on the facility of prototropic transitions in the C=N–C triad are summarized. The most facile proton transfer occurs in the *N*-benzyl derivatives, and the prototropic isomer is the more stable, the stronger the electron-acceptor power of the substituent at the sp^3-carbon atom of the azaallyl triad. The proton transfer in *N*-(α-phenethyl)-trifluoroacetimidoylphosphonates proceeds selectively, which allows preparation of enantiomerically enriched derivatives of α-aminotrifluoroethylphosphonic acid. A specific effect of substituents at the phosphorus atom on the prototropism attendant on phosphorylation of imidoyl chlorides is demonstrated.

The methylene–azomethine system is one of the least labile prototropic triads. An electron-acceptor phosphorus-containing group at the sp^2-carbon atom of the C=N–CH triad much increases the lability of the proton and thus renders such compounds labile prototropic systems [2]. Proton transfer in phosphorylated azaallyl derivatives is synthetically attractive, providing a way to converting imidoylphosphonic to biologically important α-aminophosphoryl compounds [3, 4]. The 1,3-phosphorotropic isomerization we discovered in the C=N–CH triad [5, 6] permits to perform interconversions of different α-aminophosphoryl derivatives.

In the present work we considered the effect of alkyl groups at the sp^2- and sp^3-carbon atoms of a phosphorylated azaallyl triad on the facility of 1,3-prototropic and phosphorotropic transitions, as well as the effect of substituents on the phosphorus atom on the prototropism attendant on phosphorylation of imidoyl chlorides.

As one of the synthetic approaches to imidoylphosphoryl compounds, we for the first time used the aza-Wittig reaction with acetylphosphonate **I** as the carbonyl component. It was found that imidoylphosphonate **III** formed by the reaction of oxophosphonate **I** with phosphazo compound **II** undergoes irreversible isomerization to α-phosphorylated benzalimine **IV** under the reaction conditions. The preference for the imine–imine isomerization over the imine–enamine rearrangement **III** → **V** (Scheme 1) is assignable to the possibility of effective conjugation of the C=N bond with the phenyl ring in *N*-benzylidene structure **IV**, which makes this structure favorable [2, 7].

Scheme 1.



[1] For communication XX, see [1].

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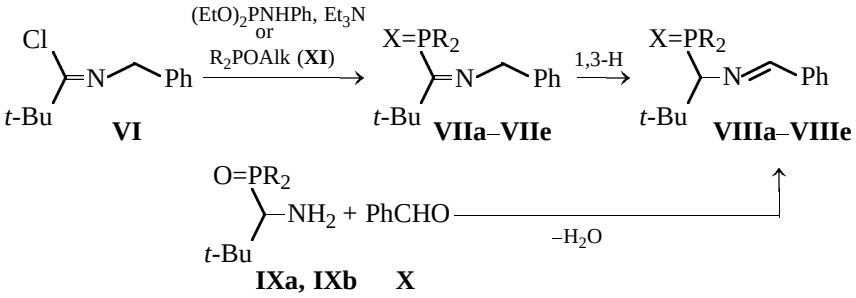
The mild conditions of the **III** → **IV** isomerization (room temperature) are probably explained by the catalytic effect of phosphazo compound **II** as a base. Evidence for this assumption comes from the fact that *P*-imidoylphosphazo compound **VIIa** undergoes spontaneous isomerization already during distillation (Scheme 2), whereas phosphonates **VIIb**–**VIId** lacking the basic phosphazo group are distilled unchanged. In the latter case, for 1,3-H shift to occur requires more rigid conditions (160–170°C) [6–9].

The most convenient synthetic approach to imidoylphosphonates **VII** is reaction of a stable imidoyl chloride **VI** containing no α-hydrogen atoms in the substituent at the imidoyl carbon atom with a P(III) derivative [6–9]. Isomeric α-phosphorylated imines **VIIIb** and **VIIIe** were obtained independently by condensation of aminophosphoryl compounds **IX** with benzaldehyde. It is important to note that compounds **VII** and **VIII** are kinetically stable and do not interconvert under usual conditions.

Scheme 2.

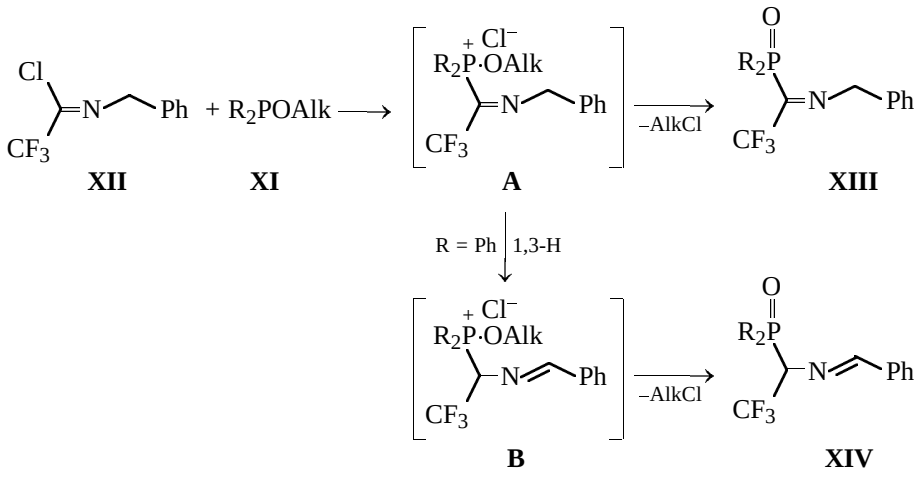


VI **VIIa–VIIe** **VIIIa–VIIIe** **IXa, IXb** **X**

VII, VIII, X = PhN (**a**), O (**b**–**e**); R = EtO (**a, b**), *i*-PrO (**c**), Me_3SiO (**d**), Ph (**e**); **IX**, R = EtO (**a**), Ph (**b**).

When heated (160–180°C), compounds **VIII** undergo phosphorotropic rather than prototropic isomerization in the C=N–C triad [5, 6, 9]. At the same time, to effect irreversible 1,3-H shift in imidoyl derivatives **VII** requires heating to 140–160°C or base catalysis. Replacement of the *tert*-butyl group (σ_I –0.02) at the imidoyl carbon atom by the electron-acceptor trifluoromethyl group (σ_I 0.43 [10]) facilitates 1,3-H shift considerably. Spontaneous prototropic isomerization in compounds **XIII** proceeds either upon their synthesis from imidoyl chloride **XII** (R = Ph) in the course of distillation or even at room temperature (slowly) [6, 11]. The strongly electron-acceptor phosphonium group at the imidoyl carbon atom favors proton transfer [2, 7, 12]. When R=Ph and Alk, quasiphosphonium intermediates are more stable, and their lifetime is sufficient for **A** to isomerize into **B** (Scheme 3) [6, 13].

Scheme 3.

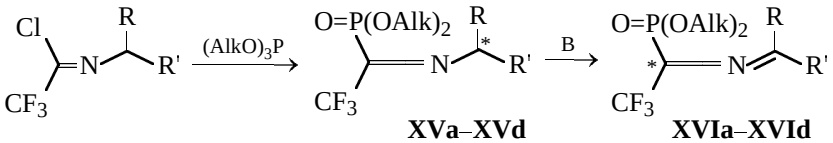


XII **XI** **A** **XIII** **B** **XIV**

R = MeO, EtO, *i*-PrO, Me_3SiO, Ph, Et.

The lability of the proton in *N*-methyl or *N*-(α-phenethyl)imidoylphosphonates is significantly decreased as compared to their *N*-benzyl analogs. Unlike easily isomerized compounds **XIII**, imidoylphosphonates **XV** are quite stable compounds and do not undergo isomerization even on heating. To effect 1,3-H shift in them requires catalysis with nitrogenous bases (Scheme 4).

Scheme 4.



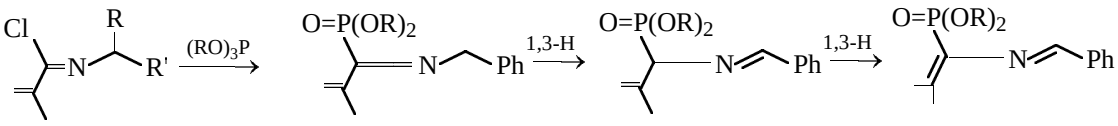
XVa–**XVd** **XVIa**–**XVId**

XV, XVI, R = R' = H, Alk = Et (**a**); R = Me, R' = Ph, Alk = Me (**b**), Et (**c**), *i*-Pr (**d**).

In the presence of triethylamine, isomerization of *N*-methyltrifluoroacetimidoylphosphonate **XVa** occurs even at room temperature, but resulting unstable methylenimine **XVIa** undergoes isomerization to give a mixture of unidentified products. Spectral identification of α-phosphorylated imine **XVIa** was carried out by comparison of its spectral characteristics (δ_P 12.3 ppm, δ_F 63.4 ppm, d.d, $^3J_{FH} \sim {}^3J_{PF}$ ~7 Hz) with those of compound **XIV**. We previously showed [11, 14] that *N*-(α-phenethyl)trifluoroacetimidoylphosphonates **XVb**–**XVd** in the presence of bases (DBU, Dabco, triethylamine) undergo irreversible 1,3-H shift to form stable α-phosphorylated *N*-alkylidenetrifluoroethylamines **XVIb**–**XVId**. The isomerization is accelerated with increasing concentration of the base. The H-shift rate constant (*k*) for phosphonate **XVc**, was estimated at 7.5×10^{-5} s^{-1} ($[Et_3N] = [\mathbf{XVc}]_0$ = 0.42 M, toluene, 90°C). The proton transfer is stereoselective and allows preparation of enantiomerically enriched phosphorus-containing analogs of trifluoroalanine [14]. Later analogous results were obtained by Xiao *et al.* [15]. Note that the referees [15] mistakenly reported a negative rotation angle for (+)-imine **XVIc** formed by isomerization of (–)-imidoylphosphonate **XVc** [14]. For imidoylphosphonates **XVb** and **XVc** first prepared by us in [11], Yuan and Zhang [16] gave wrong phosphorus chemical shifts (δ_P 2.1 and 4.37 ppm, respectively). Actually compounds **XVb** and **XVc** (δ_P –2.2 to –4.4 ppm), like other *N*-alkyl and *N*-acyltrifluoroacetimidoylphosphonates, absorb upfield with respect to H_3PO_4 (see [7] and references therein). Note that the presence of two electron-acceptor groups, phosphoryl and trifluoromethyl, at the imidoyl carbon atom of compound **XV** is a necessary condition for 1,3-H shift. Hence, replacement of the CF_3 group in compounds **XV** by phenyl (σ_I 0.10 and 0.42, respectively [10, 17]) prevents proton transfer in the C=N–C triad of the corresponding benzimidoylphosphonates [1].

In *N*-benzyl derivatives **III** and **VII** that contain methyl or *tert*-butyl groups at the C=N bond, only one electron-acceptor phosphoryl group is sufficient for proton transfer to occur (Schemes 1 and 2). This also holds true for phosphonates **XVIII** in which the imidoyl carbon atom is bound with an alkenyl radical. Here, however, consecutive proton transfer in the azaallyl and allyl triads takes place [18] (Scheme 5) to give phosphorylated azadiene **XX**. The **XVIII** → **XIX** izomerization suggests that the conjugated alkene–azomethine system is less favorable than the benzylidene one. The motive force of the **XIX** → **XX** isomerization may be formation of azadiene **XX** containing a benzylidene fragment and a longer conjugation chain.

Scheme 5.

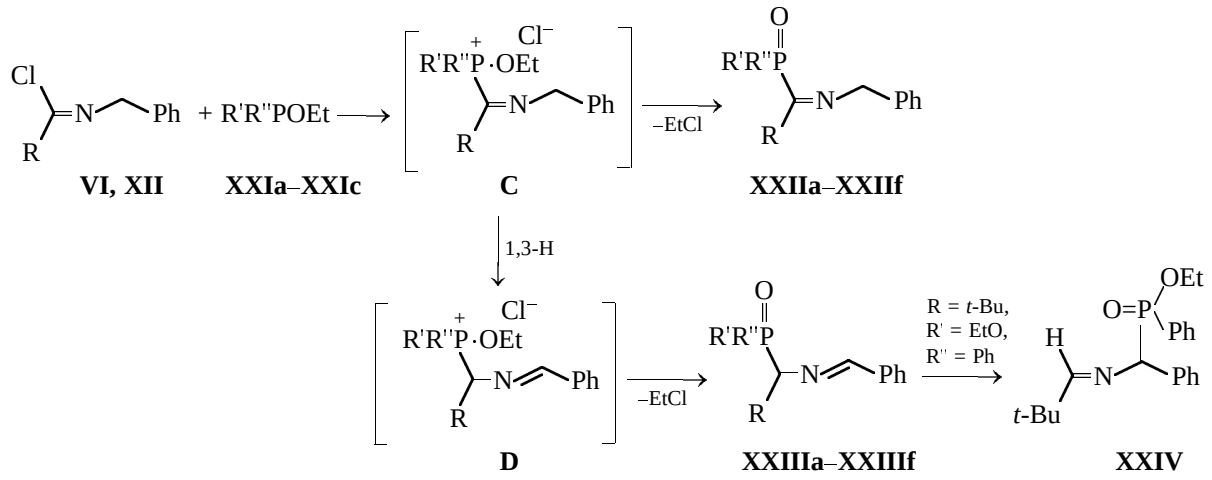


XVII **XVIII** **XIX** **XX**

R = Me, Et, *i*-Pr.

Comparison of the conditions of the 1,3-H shift in imidoylphosphonates **VIIb, VIIc**, and **XVIII** shows that the presence of the electron-acceptor alkenyl substituent (σ_I for CH_2=CMe is 0.10 [17]) at the imidoyl carbon atom favors proton transfer (CH_2=CMe > *t*-Bu). The effect of substituents on phosphorus on prototropism is clearly pronounced in the reactions of imidoyl chlorides **VI** and **XII** with triethyl phosphite, ethyl diphenylphosphinite, and diethyl phenylphosphonate (Scheme 6).

Scheme 6.



VI, XII **XXIa–XXIc** **C** **XXIIa–XXIIf**

D **XXIIIa–XXIIIf** **XXIV**

R = *t*-Bu (**VI**), CF_3 (**XII**); **XXI**, R' = R'' = EtO (**a**), Ph (**b**); R' = EtO, R'' = Ph (**c**); **XXII, XXIII**, R' = R'' = EtO, R = *t*-Bu (**a**), CF_3 (**b**); R' = R'' = Ph, R = *t*-Bu (**c**), CF_3 (**d**); R' = EtO, R'' = Ph, R = *t*-Bu (**e**), CF_3 (**f**).

The reaction of imidoyl chloride **VI** with triethyl phosphite (**XXIa**) forms imidoylphosphonate **XXIIa** which is stable in usual conditions and isomerizes at high temperature [8, 9]. The reaction with imidoyl chloride **XII** gives a mixture of prototropic isomers **XXIIb** and **XXIIIb**, the latter prevailing. In the course of distillation the **XXIIb** → **XXIIIb** isomerization completes [11]. The reaction of imidoyl chlorides **VI** and **XII** with phosphinite **XXIb** results in exclusive formation of prototropic isomers **XXIIIc** and **XXIIId** in both cases [6]. And, finally, phosphonite **XXIc** reacts with imidoyl chloride **VI** to form a mixture of prototropic isomers **XXIIe** and **XXIIIe** in a 1.4 : 1 ratio, and the reaction with trifluoroacetimidoyl chloride **XII** provides no other products than imine **XXIIIe**. Compounds **XXIIe** and **XXIIIe** were not isolated pure, since the prototropic isomerization **XXIIe** → **XXIIIe** that occurs on heating (or distillation) of the mixture of **XXIIe** and **XXIIIe** is accompanied by transfer of the phosphorus-containing group to form imine **XXIV** (cf. [5, 6, 9]).

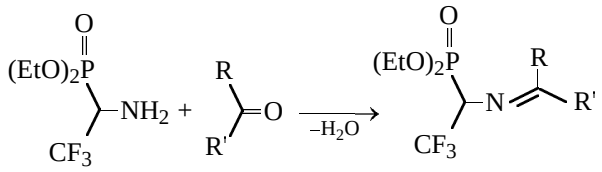
Hence, the prototropic transformations attendant in phosphorylation of imidoyl chlorides depends both on substituents at the imidoyl carbon atom and in the phosphorus reagent; however, the these effect significantly differ in nature. Substituents R at the C=N bond (Scheme 5) directly affect facility of proton transfer in the C=N–C triad (CF_3 > CH_2=CMe > Ph > *t*-Bu). As phosphorus groups R'R''P(O) in compounds **XXII** only slightly differ in electronic nature {the σ_I values of the $(EtO)_2P(O)$ and $Ph_2P(O)$ groups are 0.35 and 0.30, respectively [10]}, it is evident that the effect of substituents on phosphorus on prototropism is determined by their effect on the relative stability and, therefore, lifetime of quasiphosphonium salts **C**: (**XXIb** > **XXIc** > **XXIa**). The high electon-acceptor capacity of phosphonium groups favors proton transfer [2, 7, 12]. For this reason, at a sufficient lifetime of intermediate **C** the prototropic isomerization **C** → **D** precedes the dealkylation stage **D** → **XXIII**. A specific feature of phosphinates **XXIIe** and **XXIIf** is the presence of achiral phosphorus atom. The **XXIIe, XXIIf** → **XXIIIe, XXIIIf** or **C** → **D** → **XXIIIe, XXIIIf** isomerizations give rise to one more chiral center, a carbon atom bound with phosphorus. Compound **XXIIIf** is formed as a diastereomeric mixture (~1.3 : 1), whereas with **XXIIIf**, only one diastereomer is formed. Hence, the prototropic isomerization attendant on the phosphorylation of imidoyl chlorides **VI** and **XII** with phosphinite **XXIb** is diastereoselective. The enhancement of the diastereoselectivity in passing from **XXIIIf** to

XXIIIe is evidently explained by a stronger steric demand of the bulky *tert*-butyl group.

Evidence for the presence of two diastereomers of **XXIIIe** comes from the observation of doubled CF_3 and phosphorus signals in the ^{19}F and ^{31}P NMR spectra, as well as of CH–N proton signals in the ^1H NMR spectra. The asymmetric phosphorus atom in imidoylphosphinate **XXIIe** is responsible for the magnetic nonequivalence of the doublet proton signals of the prochiral NCH_2 group in the ^1H NMR spectra (see Experimental).

Prototropic isomers **XIV** and **XVI** can be prepared independently by condensation of aminophosphonate **XXV** with the corresponding carbonyl compounds (Scheme 7).

Scheme 7.



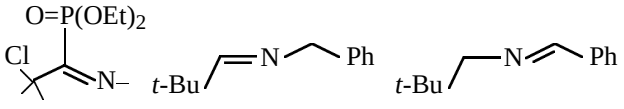
XXV **XVIe**–**XVIr**

XVI, R = H, R' = *t*-Bu (**e**), 2-thienyl (**f**), 2-HO-4-$MeOC_6H_3$ (**g**); R + R' = $(CH_2)_4$ (**h**); R = $(EtO)_2P(O)$, R' = *t*-Bu (**i**), Me (**j**) [19], Ph (**k**) [19]; R + R' = 1-R^3-5-R^4-7-R^5-2-oxoindolinyl-3-idene [20], where R^3 = R^5 = H, R^4 = H (**l**), Cl (**m**), Br (**n**), NO_2 (**o**); R^3 = H, R^4 = R^5 = Cl (**p**); R^4 = R^5 = H, R^3 = $PhCH_2$ (**q**), 2-$FC_6H_4CH_2$ (**r**).

Independently of substituents R and R', prototropic isomers **XIV** and **XVIb**–**XVIr** are stable compounds that do not convert into imidoyl isomers **XIII** and **XV** under heating or nitrogenous base catalysis. This also relates to compounds **XVIl**–**XVIr** whose imine carbon atom is incorporated into the isatine heteroring containing the electron-acceptor C=O group in the α position [20].

Substituents at the carbon atoms of the C=N–C triad exert a considerable effect both on thermodynamic preference of the prototropic isomers and their tendency for 1,3-H shift. Electron-acceptor substituents facilitate proton transfer, and, other conditions being equal, an isomer that has the strongest electron-acceptor substituents at the sp^3-carbon atom, is the most thermodynamically favorable [2, 7, 21]. Hence, proton transfer in (*N*-methyltrifluoroacetimidoyl)-phosphonate in the presence of Et_3N takes place at 20°C (Scheme 4), and imidoylphosphonate **XXVI** with the weaker electron-acceptor Me_2CCl group at the imidoyl carbon atom is stable under analogous, as well as more rigid conditions [22]. Contrary to easily isomerized *N*-benzimidoylphosphonates **VII**, *N*-benzylimine **XXVII** containing no phosphorus at the imine carbon atom is insusceptible to proton transfer even on heating in the presence of nitrogenous bases (DBU, Dabco), even though *N*-benzylidene isomer **XXVIII** is evidently thermodynamically more favorable.

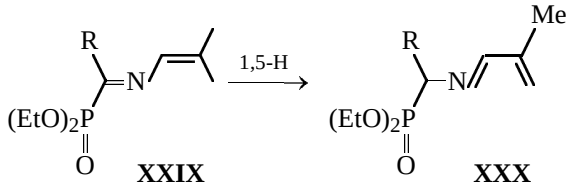
The activating effect of electron-acceptor substituents at the imidoyl carbon atom on proton transfer



XXVI **XXVII** **XXVIII**

also reveals itself in vinylogs of phosphorylated azaallyl compounds **XXIX** (CF_3 > Ph), where the imidoyl carbon atom and migrating proton are intervened by an additional C=C fragment (Scheme 8) [23].

Scheme 8.



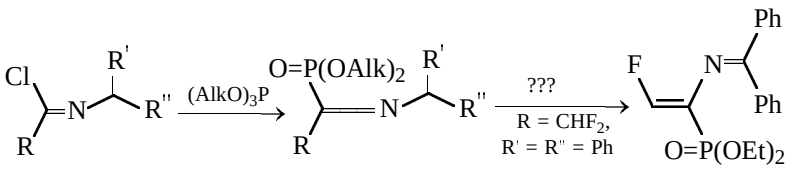
XXIX **XXX**

R = CF_3, Ph.

Comparison of Schemes 3, 4, and 9 demonstrates the effect of substituents in the *N*-alkyl radical of imidoylphosphonates on prototropism. Compound **XIII** with an *N*-benzyl group easily isomerizes even in the absence of bases (Scheme 3). Introduction of the electron-donor methyl (σ_I –0.05) and the electron-acceptor phenyl group (σ 0.1) [17] complicates isomerization. To effect the **XV** → **XVI** conversion requires base catalysis (Scheme 4) [11, 14], and in

compound **XXXIb** (Scheme 9) no proton transfer was found [24]. Treatment of compound **XXXIb** with base does not cause isomerization but leads to dehydrofluorination to form azadiene **XXXII** (Scheme 9) [24]. Benzimidoylphosphonates **XXXIc** with two electron-acceptor trifluoromethyl groups at the sp^3-carbon atom are also not prone to proton transfer [1]. It is evident that the formation of a favorable benzylidene structure like **XIV**, where there are optimal conditions for conjugation of the C=N bond with the aryl radical, is primarily responsible for the easy isomerization of *N*-benzylimidoylphosphonates.

Scheme 9.

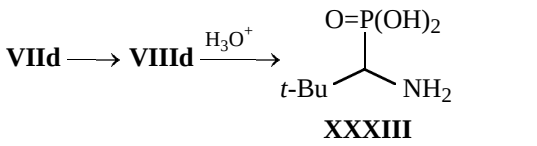


XXXIa–**XXXIc** **XXXII**

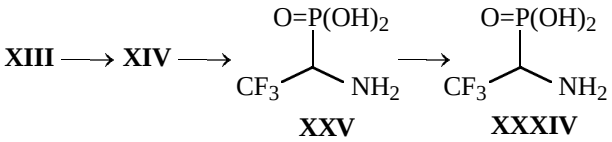
R' = R'' = Ph, R = CF_3 (**a**), CHF_2 (**b**); R = Ph, R' = R'' = CF_3 (**c**).

Hence, in terms of the tendency for prototropic transformations the above-described systems can be arranged in the following series: **XIII** > **XVIII** > **VII** > **XV** > **XXVI,XXVII, XXXI; XXIIb, XXIId, XXIIf** > **XXIIa, XXIIc, XXIIf**. Proton transfer in *N*-benzylalkanimidoylphosphonates **III, VII, XIII,** and **XV** can be used as a synthetic approach to α-aminoalkylphosphonates and phosphonic acids [1, 20] (Schemes 2–4, 6, 10).

Scheme 10.



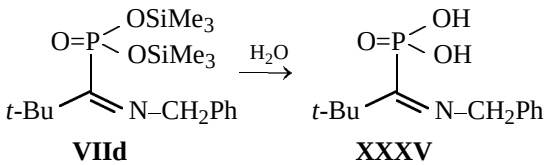
XXXIII



XXV **XXXIV**

Mild hydrolysis of imine **VIId** leads to compound **XXXV**, a rare representative of imidoylphosphonic acids (Scheme 11).

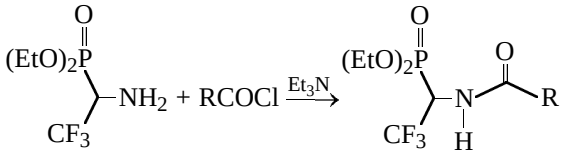
Scheme 11.



VIId **XXXV**

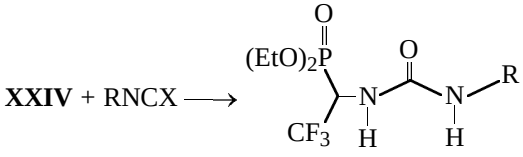
Trifluoroethylaminophosphonate **XXV** with the electron-acceptor trifluoromethyl group is comparatively stable in usual conditions and can be used for preparing functional derivatives with a trifluoroethylphosphonic acid fragment. Schemes 7 and 12 demonstrate the possible syntheses of imines, *N*-acylaminophosphonates, and C-phosphorylated ureas.

Scheme 12.



XXIV **XXXVIa**–**XXXVIf**

XXXVI, R = Ph (**a**), 4-FC_6H_4 (**b**), 2,4-$Cl_2C_6H_3$ (**c**), 3,5-$(NO_2)_2C_6H_3$ (**d**), 3,4,5-$(MeO)_3C_6H_2$ (**e**), 2-thienyl.



XXXVIIa–**XXXVIIc**

XXXVII, R = 3,4-$Cl_2C_6H_3$, X = O (**a**); R = cyclohexyl, X = O (**b**); R = Ph, X = S (**c**).

It is important to note that the synthesis of α-aminoalkylphosphoryl derivatives by means of prototropic rearrangements is especially attractive for phosphorylation of N-benzyl-substituted imidoyl chlorides (Schemes 2, 3, 5, and 6). In this case, the proton

transfer in the C=N–C triad takes place just under phosphorylation conditions. A specific feature of phosphorus nucleophiles is the ability of phosphorus to give derivatives of different coordination. Phosphorylation may be accompanied by changes both in valence and in coordination. It is these circumstances, specifically relative stability of highly electron-acceptor intermediates of the Arbuzov reaction, like **A** and **C** (Schemes 3 and 6), that are responsible for the fact that proton transfer may take place at the stage of quasiphosphonium intermediates, and the established regularities of the effect of substituents on the phosphorus and carbon atoms on the prototropism in the C=N–C triad allow one to control this process.

EXPERIMENTAL

The IR spectra were measured on a UR-20 spectrometer. The ^{1}H, ^{19}F, and ^{31}P NMR spectra were measured on a Varian VXR-300 spectrometer at 299.95, 282.20, and 121.42 MHz, respectively. The chemical shifts were measured against internal TMS (^{1}H) and $CFCl_3$ (^{19}F) and external 85% phosphoric acid (^{31}P).

3-(Diethoxyphosphinoyl)-1-phenyl-2-azabut-1-ene (IV). To a solution of 6.8 mmol of phosphazo compound **II** in 15 ml of benzene, a solution of 6.8 mmol of acetylphosphonate **I** was added dropwise at 5°C. The reaction mixture was heated to room temperature and left to stand for 2 h. Benzene was evaporated, and the residue was extracted with petroleum ether (40–60°C, 5 × 10 ml). The solvent was evaporated, and the residue was distilled in a vacuum. Yield 54%, bp 133–134°C (0.07 mm Hg). IR spectrum (CCl_4), ν, cm^{-1}: 1047 (P–O–C), 1275 (P=O), 1674 (C=N). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.31 t and 1.33 t (6H, *Me*CH_2), 1.57 d.d (3H, *Me*CH, $^{3}J_{HP}$ 18 Hz, $^{3}J_{HH}$ 7 Hz), 3.88 d.q (1H, CHP, $^{2}J_{HP}$ ~15, $^{3}J_{HH}$ 7 Hz), 4.17 m (4H, OCH_2), 7.4 m (3H, Ph), 7.7 m (2H, Ph), 8.34 d (1H, CH=N, $^{4}J_{HP}$ 4.8 Hz). ^{31}P NMR spectrum ($CDCl_3$): δ_P 25.8 ppm. Found, %: N 5.18; P 11.50. $C_{13}H_{20}NO_3P$. Calculated, %: N 5.20; P 11.50.

(3-Diethoxyphosphinoyl)-4,4,4-trifluoro-2-azabut-1-ene (XVa). A solution of 20 mmol of *N*-methyltrifluoroacetimidoyl chloride and 20 mmol of triethyl phosphite in 4 ml of toluene was heated in a sealed ampule at 110-120°C for 4 h and then distilled in a vacuum. Yield 55%, bp 94–97°C (12 mm Hg), n_D^{20} 1.4004, δ_P –4.4 ppm {published data [25]: bp 95–97°C (12 mm), n_D^{20} 1.4005, δ_P –5.3 ppm}.

Isomerization of *N*-methyltrifluoroacetimidoylphosphonate (XVa) under the action of bases. Imidoylphosphonate, 0.1 g, and 0.2 ml of triethylamine were mixed at 20°C, and the mixture was studied by NMR spectroscopy. After 2.5 h, the signal of starting phosphonate **XVa** (–4.4 ppm) disappeared. Signals of imine **XVIa** (δ_P 12.3 ppm), aminophosphonate **XXV** (δ_P 17.5), and unidentified compounds (δ_P 0.15 and 32.9 ppm) were detected in a 15 : 2 : 1 : 1 ratio. A day later, the signals of imine **XVIa** disappeared, and unidentified signals at δ_P 19.0 and 21.7 ppm appeared.

Treatment of imidoylphosphonate **XVa** with Dabco or DBU in benzene at 20°C leads to the similar results: First phosphonate **XVa** isomerizes into imine **XVIa** and then the latter product converts into unidentified compounds.

(–)-2-(Diisopropoxyphosphinoyl)-1,1,1-trifluoro-4-phenyl-3-azabut-2-ene (XVd) was prepared from (–)-*N*-(α-phenethyl)trifluoroacetimidoyl chloride and triisopripyl phosphite analogously to [14], yield 60%, bp 104–105°C (0.05 mm Hg), $[\alpha]_D$ –63.3° (*c* 10, benzene). ^{31}P NMR spectrum ($CHCl_3$), δ_P –6.4 ppm.

(+)-4-(Diisopropoxyphosphinoyl)-5,5,5-trifluoro-2-phenyl-3-azabut-2-ene (XVId). To a solution of 1.3 g of imidoylphosphonate **XVd** in 10 ml of toluene, 0.12 g of Dabco was added, and the resulting mixture was heated at 100°C for 3 h. Removal of the solvent and distillation gave 65% of enantiomerically enriched phosphonate **XVId**, bp 108–109°C (0.06 mm Hg), $[\alpha]_D$ +31.2° (*c* 5.5, benzene). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.30, 1.32, 1.35 all d (12H, C*H*$_3$CH, $^{3}J_{HH}$ 6 Hz), 2.39 d (3H, C*H*$_3$C=, $^{5}J_{HP}$ 3 Hz), 4.64 d.q (1H, CHP, $^{2}J_{HP}$ ~17 Hz, $^{3}J_{HF}$ 8.5 Hz), 4.70 m (1H) and 4.81 m (1H), both (OCH_3), 7.4 m (3H, Ph), 7.91 m (2H, Ph). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 16.12 s (*Me*C), 23.53 d (*Me*CH, $^{3}J_{CP}$ 5.7 Hz), 23.89 d (*Me*CH, $^{3}J_{CP}$ 5.2 Hz), 24.08 d (*Me*CH, $^{3}J_{PC}$ 4 Hz), 34.32 d (*Me*CH, $^{3}J_{CR}$ 4 Hz), 63.52 d.q (CHP, $^{1}J_{CP}$ 155 Hz, $^{2}J_{CF}$ 28 Hz), 72.58 d (CHO, $^{2}J_{CP}$ 8 Hz), 123.79 q.d (CF_3, $^{1}J_{CF}$ 279 Hz, $^{3}J_{CP}$ 3 Hz), 127.27 and 128.27 s (*o*- and *m*-C_{Ph}), 130.56 (*p*-C_{Ph}), 139.84 (*ipso*-C_{Ph}), 171.70 d (C=N, $^{3}J_{CP}$ 11 Hz). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 11.34. Found,%: F 15.57; P 8.86. $C_{16}H_{23}F_3NO_3P$. Calculated,%: F 15.60; P 8.48.

5-(Diethoxyphosphinoyl)-2,2-dimethyl-6,6,6-trifluoro4-azahex-3-ene (XVIe). A mixture of 20 mmol of aminophosphonate **XXV** and 22 mmol of pivalaldehyde was heated at 65–70°C for 5 h, and the product was distilled in a vacuum. Yield 58%, bp 54–56°C (0.05 mm Hg), n_D^{20} 1.4076. ^{1}H NMR spectrum (CCl_4), δ, ppm: 1.43 s (9H, *t*-Bu), 1.67 t (6H, *Me*CH_2), 3.67–4.80 m (5H, OCH_2+CHP), 7.98 d (1H, CH=N, $^{4}J_{HP}$ 4.2 Hz). Found, %: N 4.88; P 10.14. $C_{11}H_{21}F_3 \cdot NO_3P$. Calculated, %: N 4.62; P 10.21.

3-(Diethoxyphosphinoyl)-4,4,4-trifluoro-1-(2-thienyl)-2-azabut-1-ene (XVIf). Equimolar mixture of aminophosphonate **XXV** and 2-thienylcarbaldehyde was kept for 1 day at room temperature in the presence of a catalytic amount of *p*-toluenesulfonic acid. The product was distilled in a vacuum. Yield 36%, bp 127–128°C (0.3 mm Hg), n_D^{20} 1.4980. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.3 m (6H, *Me*CH_2), 4.1 m (5H, OCH_2 + CHP), 7.0 m (2H, thienyl), 8.47 d (1H, CH=N, $^4J_{HP}$ 3.8 Hz). ^{31}P NMR spectrum ($CHCl_3$), δ_P, ppm: 12.1. ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –68.3. Found, %: N 4.35; P 9.46; S 9.76. $C_{11}H_{15}F_3NO_3PS$. Calculated,%: N 4.25; P 9.41; S 9.74.

3-(Diethoxyphosphinoyl)-1-(2-hydroxy-4-methoxyphenyl)-4,4,4-trifluoro-2-azabut-1-ene (XVIg). A solution of equimolar amounts of aminophosphonate **XXV** and 2-hydroxy-4-methoxybenzaldehyde in benzene was refluxed with a Dean–Stark trap for 10 h. The solvent was evaporated, and the residue was kept in an oil pump vacuum at 20°C. Yield of the target product 75%. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.33 t and 1.37 t (6H, *Me*CH_2), 3.79 s (3H, MeO), 4.1–4.3 m (5H, CH_2O + CHP), 6.82 d (1H, 3-H_{Ar}, $^4J_{HH}$ 3.3 Hz), 6.93 d (1H, 6-H_{Ar}, $^3J_{HH}$ 9 Hz), 7.02 d.d (1H, 5-H_{Ar}, $^3J_{HH}$ 9, $^4J_{HH}$ 3.3 Hz), 8.45 d (1H, CH+N, $^4J_{HP}$ 3.6 Hz), 11.6 br (NH). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 11.9. ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –89.0, $^3J_{FH}$ ~ $^3J_{FP}$ ~7.5 Hz. Found, %: F 15.61; P 8.05. $C_{14}H_{19}F_3NO_5P$. Calculated, %: F 15.43; P 8.39.

Diethyl 1-(cyclopentylideneamino)-2,2,2-trifluoroethylphosphonate (XVIh) was prepared similarly to compound **XVIg**. Yield 70%. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.3 t (6H, *Me*CH_2), 1.7–2.7 m (8H, cyclopentyl), 4.1–4.4 m (5H, CH_2O + CH_2P). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 14.1. ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –68.8 d.d, $^3J_{FH}$ ~ $^3J_{FP}$ ~8.8 Hz. Found, %: F 18.13; P 10.36. $C_{11}H_1F_3NO_3P$. Calculated, %: F 18.92; P 10.28. According to the ^{19}F and ^{31}P NMR spectra, the product contains about 20 mol% of a compound which is probably the enamine isomer of phosphonate **XVIh**: δ_P 13.8 ppm, δ_F –68.5 ppm.

1-Phenyl-3-[ethoxy(phenyl)phosphinoyl-4,4,4-trifluoro-2-azabutene-1 (XXIIIf). An equimolar mixture of imidoyl chloride **XII** and diethyl phenylphosphonite **XXIc** was heated under the inert atmosphere until the completion of gas evolution at 70–110°C for 1 h. The resulting mixture was distilled in a vacuum to give the target product in 48% yield, bp 185–190°C (0.3 mm Hg), crystallizes on handling. ^{1}H NMR spectrum (acetone-d_6) δ, ppm: 1.28–1.47 m (3H, CH_3CH$_2$), 3.9–4.5 m (3H, OCH_2 + CHP), 7.3–7.9 m (10H, Ph), 8.30 d (0.43 H, CH=N, $^4J_{HP}$ 3.8 Hz), 8.40 d (0.57 H, CH=N, $^4J_{HP}$ 3.8 Hz). ^{31}P NMR spectrum (acetone-d_6), δ_P. ppm: δ_1 31.61, δ_2 34.31, $\delta_1:\delta_2$ 1.3:1. ^{19}F NMR spectrum (acetone-d_6), δ_F, ppm: δ_1 –69.55, δ_2 –69.39. Found, %: F 16.49; P 8.67. $C_{17}H_{17}F_3NO_2P$. Calculated, %: F 16.04; P 8.72.

Reaction of imidoyl chloride VI with diethyl phenylphosphonite (XXIc). Equimolar mixture of imidoyl chloride **VI** and diethyl phenylphosphonite **XXIc** was heated in an inert atmosphere at 60–110°C until gas evolution was no longer observed (2 h). Vacuum distillation gave a fraction with bp 168–175°C (0.1 mm Hg), yield 69%, colorless viscous liquid. According to the ^{1}H NMR spectrum (acetone-d_6–CCl_4), it is a mixture of prototropic isomers **XXIIe** and **XXIIIe** and unidentified admixtures. Imidoylphosphonate **XXIIe**, ^{1}H NMR spectrum, δ, ppm: 1.04 s (9H, Me_3C), 4.58 d (1H, $^4J_{HP}$ 3.5 Hz) and 4.67 d (1H, $^4J_{HP}$ 4.0 Hz) (NCH_4AH_B). Imine **XXIIId**, ^{1}H NMR spectrum, δ, ppm: 1.11 s (9H, Me_3C), 3.47 d (1H, CHP, $^2J_{HP}$ 15 Hz), 8.12 d (1H, CH=N, $^4J_{HP}$ 4.5 Hz). The Ph and OCH_2 signals of isomers **XXIIe** and **XXIIIe** overlap. Upon heating of the mixture (140–160°C), CHP proton signals of two diastereomers of phosphorotropic isomer **XXIV** appear, ppm: δ_1 4.86 d ($^2J_{HP}$ 16 Hz); δ_2 4.94 d ($^2J_{HP}$ 17 Hz).

(1-Amino-2,2-dimetylpropyl)phosphonic acid (XXXIII). A mixture of 1.5 g *N*-(1-chloro-2,2-dimethylpropylidene)benzylamine and 2.4 g of tris(trimethylsilyl) phosphite was heated for 1 h at 160°C and distilled in a vacuum to obtain 1.87 g (66%) of imidoylphosphonate **VIId** [9], bp 109–111°C (0.05 mm Hg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.21 s (18H, Me_3Si), 1.27 s (9H, Me_3C), 4.92 s (2H, CH_2), 7.3 m (5H, Ph). ^{31}P NMR spectrum (CCl_4): δ_P –15.67 ppm. Compound **VIId** was heated for 1 h at 180°C. Under these conditions, it isomerized into compound **VIIId** [9]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.15 and 0.19 s (18H, Me_3Si), 1.05 s (9H, Me_3C), 3.15 d (1H, CHP, $^2J_{HP}$ 15.0 Hz), 7.2, 7.7 m (5H, Ph), 8.12 d (1H, CH=N, $^4J_{HP}$ 7.8 Hz). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 4.88 d $^2J_{HP}$ 14.7 Hz, $^4J_{HP}$ 6.0 Hz). Phosphonate **VIIId** was treated with 12 ml of 6N HCl and extracted with chloroform (3 × 5 ml). The aqueous layer was evaporated, the dry residue was dissolved in 12 ml of anhydrous ethanol, and 0.33 ml of propylene oxide was added. The precipitate that formed was filtered off. Yield 0.56 g (72%), mp 259–260°C (from aqueous ethanol). ^{1}H NMR spectrum (CF_3COOD), δ_P, ppm: 0.93 s (9H, CH_3), 3.32 d (1H, CH, $^2J_{HP}$ 16.0 Hz). ^{31}P NMR spectrum (H_2O), δ_P, ppm: 11.99 d ($^2J_{PH}$ 16.0 Hz). Found, %: C 35.88;

H 8.27; N 8.41; P 18.53. $C_5H_{14}NO_3P$. Calculated, %: C 35.93; H 8.46; N 8.38; P 18.53.

(1-Amino-2,2,2-trifluoroethyl)phosphonic acid (XXXIV). A mixture of 2.6 g of *N*-benzyltrifluoroacetimidoyl chloride and 2.1 g of triethyl phosphite was heated for 3 h at 120°C and then distilled in a vacuum to obtain a mixture of isomers **XIII** and **XIV**, yield 72%, bp 120–125°C (0.7 mm Hg). The mixture was heated for 2 h at 160°C, after which 15 ml of 6N HCl was added, the resulting mixture was stirred for 20 min, and the oily substance that floated was extracted with ether (3 × 5 ml). The aqueous phase was refluxed for 6 h and evaporated in a vacuum. The dry residue was dissolved in 6 ml of anhydrous ethanol, and 0.25 g of propylene oxide was added. The precipitate that formed was filtered off to obtain 0.91 g (60%) of aminophosphonic acid **XXXIV**, mp 227–227.5°C. ^{1}H NMR spectrum (D_2O), δ, ppm: 3.83 d.d (1H, CH_2, $^2J_{HP}$ 15.5 Hz, $^3J_{HF}$ 8.6 Hz). ^{31}P NMR spectrum (D_2O), δ_P, ppm: 1.9 d.q, $^2J_{PH}$ 15.5 Hz, $^3J_{PF}$ 5.9 Hz. ^{19}F NMR spectrum (D_2O), δ_F, ppm: –67.8 d.d, $^3J_{FH}$ 8.7 Hz, $^3J_{PF}$ 5.9 Hz. Found, %: C 13.68; H 3.04; F 31.79; N 7.79; P 17.28. $C_2H_5F_3 \cdot NO_3P$. Calculated, %: C 13.42; H 2.81; F 31.83; N 7.28; P 17.32.

(***N*-Benzyl-2,2-dimethylpropanimidoyl)phosphonic acid (XXXV)** is formed on handling of imidoylphosphonate **VIId** in air. mp 16073172°C. ^{1}H NMR spectrum (CD_3OD), δ, ppm: 1.25 s (9H, Me), 4.11 s (2H, CH_3), 7.44 m (5H, Ph). ^{31}P NMR spectrum (CD_3OD): δ_P –1.5 ppm. Found, %: N 5.46; P 12.01. $C_{12}H_{18}NO_3P$. Calculated, %: N 5.49; P 12.13.

Diethyl (1-acylamino-2,2,2-trifluoroethyl)phosphonates XXXVIa–XXXVIc. To a solution of aminophosphonate **XXV** in ether, equivalent amounts of triethylamine and the corresponding benzoyl chloride were successively added. A day later, the resulting mixture was filtered, the solvent was removed from the filtrate, and the residue was crystallized from petroleum ether.

Diethyl (1-benzoylamino-2,2,2-trifluoroethyl)-phosphonate (XXXVIa). Yield 86%, mp 93–94°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.31 t and 1.37 t (6H, *Me*CH_2), 4.22 m (4H, OCH_2), 5.38 m (1H, CHP), 6.03 d (1H, NH, $^3J_{HH}$ 9 Hz), 7.48 m (2H, Ph), 7.57 m (1H, Ph), 7.8 m (2H, Ph). ^{31}P NMR spectrum (benzene), δ_P, ppm: 13.0. ^{19}F NMR spectrum, δ_F, ppm: –68.6. Found, %: N 4.20; P 9.17. $C_{13}H_{17}F_3 \cdot NO_4P$. Calculated, %: N 4.13; P 9.13.

Diethyl [2,2,2-trifluoro-1-(4-fluorobenzoylamino)ethyl]phosphonate (XXXVb. Yield 79%, mp 94–95°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.31 t and 1.38 t (6H, *Me*CH_2), 4.23 m (4H, OCH_2), 5.36 m (1H, CHP), 7.08 d (1H, NH, $^3J_{HH}$ 10 Hz), 7.16 m (2H, Ph). 7,90 m (2H, Ph). ^{31}P NMR spectrum (THF), δ_P, ppm: 13.7. ^{19}F NMR spectrum (THF), δ_F, ppm: –68.5 (3F, CFd3), –108.79 (1F, FC_6H_4). Fou nd, %: N 4.12; P 8.43. $C_{13}H_{16}F_4NO_4P$. Calculated, %: N 3.92; P 8.67.

Diethyl [1-(2,4-dichlorobenzoylamino)-2,2,2-trifluoroethyl]phosphonate (XXXVIc). Yield 70%, mp 102–103°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.34 t (6H, *Me*CH_2), 4.21 m (4H, OCH_2), 5.29 m (1H, CHP), 7.20 d (1H, NH, $^3J_{HH}$ 8 Hz), 7.35 d (1H, Ph), 7.47 s (1H, Ph), 7.52 d (H, Ph). ^{31}P NMR spectrum ($CHCl_3$): δ_P 13.33 ppm. ^{19}F NMR spectrum ($CHCl_3$): δ_F –68.0 ppm. Found, %: Cl 17.60; P 7.78. $C_{13}H_{15} \cdot F_3NO_4P$. Calculated, %: Cl 17.37; P 7.59.

Diethyl [1-(3,5-dinitrobenzoylamino)-2,2,2-trifluoroethyl]phosphonate (XXXVId). Equimolar amounts of aminophosphonate **XXV**, triethylamine, and 3,5-dinitrobenzoyl chloride were mixed in benzene at room temperature. A day later, the precipitate that formed was filtered off, washed on the filter with water from triethylamine hydrochloride, and crystallized from ethanol. Yield 71%, mp 132–133°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.29 t and 1.37 t (6H, *Me*CH_2), 4.22 m (4H, OCH_2), 5.45 m (1H, CHP), 9.20 s (3H, Ph), 9.26 d (1H, NH, $^3J_{HH}$ 9.6 Hz). ^{31}P NMR spectrum ($CHCl_3$): δ_P 12.34 ppm. ^{19}F NMR spectrum (acetone-d_6): δ_F –67.38 ppm. Found, %: P 7.26. $C_{13}H_{15}F_3N_3O_8P$. Calculated, %: P 7.22.

Diethyl [1-(3,4,6-trimethoxybenzoylamino)-2,2,2-trifluoroethyl]phosphonate (XXXVIe). Equimolar amounts of aminophosphonate **XXV**, triethylamine, and 3,4,5-trimethoxybenzoyl chloride were heated in benzene at 50–60°C for 6 h. The precipitate that formed was filtered off, and the solvent was removed from the filtrate. The oily residue was several times extracted with hot petroleum ether. The oil that precipitated on cooling was dissolved in ethanol, filtered, and the solvent was removed. The residue was triturated with petroleum ether until crystals formed. Yield 33%. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.30 t and 1.38 t (6H, *Me*CH_2), 3.88 s (3H, MeO), 4.1–4.3 m (4H, OCH_2), 5.31 m (1H, CHP), 6.8 d.d (1H, NH, $^3J_{HH}$ 9.5 Hz, $^3J_{HP}$ 3 Hz), 7.04 s (2H, Ph). Found, %: P 7.21. $C_{16}H_{23}F_3NO_7P$. Calculated, %: P 7.21.

Diethyl [2,2,2-trifluoro-1-(2-thienylamino)-ethyl]phosphonate (XXXVIf). A mixture of equimolar amounts of aminophosphonate **XXV**, triethylamine, and 2-thiophenecarbonyl chloride was refluxed in benzene for 4 h. The resulting mixture was filtered, the solvent was evaporated, and the crystalline residue

was washed on the filter with water and crystallized from a petroleum ether–benzene mixture. Yield 86%, mp 126.5–128°C. ^{31}P NMR spectrum ($CDCl_3$), δ, ppm: 1.27 t and 1.33 t (6H, *Me*CH_2), 4.21 m (4H, OCH_2), 5.42 m (1H, CHP), 7.19 t (1H, thienyl), 7.82 d (1H, thienyl), 8.06 d (1H, thienyl), 8.48 d (1H, NH, $^3J_{HH}$ 10 Hz). ^{31}P NMR spectrum (acetone-d_6): δ_P 14.81 ppm. Found, %: P 8.61; S 9.60. $C_{11}H_{15}F_3NO_4PS$. Calculated, %: P 8.97; S 9.29.

***N*-[1-(Diethoxyphosphinoyl)-2,2,2-trifluoroethyl]*N'*-(3,4-dichlorophenyl)urea (XXXVIIa)**. Equimolar amounts of aminophosphonate **XXV** and 3,4-dichlorophenyl isocyanate were mixed in benzene. A day later, the crystals that formed were filtered off and washed with benzene. Yield 83%, mp 198–201°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.33 t and 1.47 t (6H, *Me*CH_2), 4.23 m and 4.32 d.q (4H, OCH_2), 5.11 m (1H, CHP), 7.04 d (1H, CHN*H*, $^3J_{HH}$ 11 Hz), 7.32 m (2H, Ph), 7.55 s (1H, Ph), 8.48 s (1H, NHAr). ^{31}P NMR spectrum ($CHCl_3$): δ_P 14.72 ppm. Found, %: Cl 16.83; P 7.52. $C_{12}H_{16}Cl_2F_3N_2O_4P$. Calculated, %: Cl 18.76; P 7.32.

***N*-[1-(Diethoxyphosphinoyl)-2,2,2-trifluoroethyl]-*N'*-cyclohexylurea (XXXVIIb)**. Equimolar amounts of aminophosphonate **XXV** and cyclohexyl isocyanate were refluxed in benzene for 6 h. The solvent was removed, and the oily residue was washed with several portions of petroleum ether and precipitated with water from ethanol. Yield 32%. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.11 m (3H, cyclohexyl), 1.31 t and 1.39 t (6H, *Me*CH_2 + 1H, cyclohexyl), 1.63 m (4H, cyclohexyl), 1.90 m (2H, cyclohexyl), 3.61 m (1H, cyclohexyl), 4.12 m (4H, OCH_2), 5.04 m (1H, CHP), 5.87 d (1H, NH–cyclohexyl, $^3J_{HH}$ 7 Hz), 6.67 d (1H, NH, $^3J_{HH}$ 10 Hz). Found,%: N 7.89; P 8.65. $C_{13}H_{24}F_3N_2O_4P$. Calculated,%: N 7.77; P 8.59.

***N*-[1-(Diethoxyphosphinoyl)-2,2,2-trifluoroethyl]-*N'*-phenylthiourea (XXXVIIc)**. Equimolar amounts of aminophosphonate **XXV** and phenyl isothiocyanate were mixed at room temperature. A day later, the crystalline material was thoroughly washed with petroleum ether. Yield 92%, mp 141–144°C. ^{1}H NMR spectrum ($CDCl_3$, external HMDS), δ, ppm: 1.77 m (6H, *Me*CH_2), 4.67 d.q (4H, OCH_2), 6.74 m (1H, CHP), 7.40–8.10 m (5H, Ph), 8.53 d (1H, NH, $^3J_{HH}$ 10 Hz), 9.83 s (1H, NHPh). Found, %: N 7.71; P 8.63; S 8.88. $C_{13}H_{18}F_3N_2O_3PS$, Calculated, %: N 7.56; P 8.36; S 8.66.

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