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Sigmatropic Isomerizations in Azaallyl Systems: XXII.[1] 1,3-Proton Transfer in (*N*-Alkyltrifluoroacetimidoyl)phosphonates

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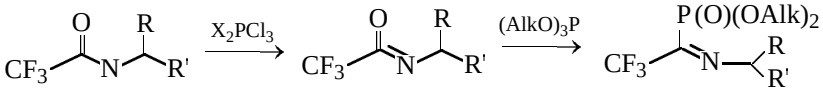
Abstract—The reaction of *N*-alkyltrifluoroacetimidoyl chlorides with trialkyl phosphites leads to corresponding imidoylphosphonates $CF_3C[P(O)(OAlk)_2]=NCH_2R$. These compounds undergo irreversible 1,3-H shift catalyzed by nitrogenous bases to give phosphorylated imines $CF_3CH[P(O)(OAlk)_2]N=CHR$. The tendency for prototropism increases with increasing electronegativity of substituents R: CF_3 > CH_2OMe > H > Me. *N*-Cyclopentyl analogs of the obtained compounds show no tendency for prototropism. Imidoylphosphonates exist mainly as *Z* isomers [*Z*/*E* ~(6–10) : 1].

Imidoylphosphonates are promising synthetic precursors of biologically important derivatives of α-aminophosphonic acids. As they are the "oxidized" form of α-aminophosphonates, reduction of the C=N bond (conversion PC=N → PCHN) is a way of their transformation into α-aminophosphoryl derivarives. Intramolecular proton transfer that simulates biochemical transamination allows this process to be performed in the absence of a foreign reducing agent. In previous communications of this series we showed that 1,3-H transfer is characteristic of benz- [2] and some alkanimidoylphosphonates [1]. In the present work we synthesized (*N*-alkyltrifluoroacetimidoyl)phosphonates **I** and considered the effect of substituents in the *N*-alkyl radical on the 1,3-H transfer. The electron-acceptor and simultaneously fairly chemically inert trifluoromethyl group on the sp^2-carbon atom of compound **I** favors proton transfer and thus allows synthesis of phosphorus analogs of trifluoroalanine that act as enzyme inhibitors [1, 3].

Imidoylphosphonates **I** were prepared by reaction of trialkyl phosphites with imidoyl chlorides **II** obtained by chlorination of trifluoroacetamides **III** (Scheme 1).

Scheme 1.



IIIa–IIIg **IIa–IIg** **Ia–Ik**

I, R = R' = H, Alk = Et (**a**) [1], *i*-Pr (**b**); Alk = Et, R' = H, R = Me (**c**), CH_2OMe (**d**), CF_3 (**e**), Ph (**f**) [4]; Alk = *i*-Pr, R' = H, R = CF_3 (**g**); Alk = Me, R = H, R' = Ph (**h**) [4]; R = Me, R' = Ph, Alk = Et (**i**) [4, 5], *i*-Pr (**j**) [1]; Alk = Et, R + R' = $(CH_2)_4$ (**k**). **II, III**, R = H, R' = H (**a**) [1], Me (**b**), CH_2OMe (**c**), CF_3 (**d**), Ph (**e**) [4]; R + R' = $(CH_2)_4$ (**f**); R = Me, R' = Ph (**g**) [4, 5].

Compounds **II** react with trialkyl phosphites under rather rigid conditions (refluxing in toluene or heating without solvent at 100–130°C). The reaction is quite sensitive to admixtures in imidoyl chlorides **II**. Imidoylphosphonates **I** are formed as mixtures of *E* and *Z* isomers. Signals of the isomers were assigned by comparing their spectral characteristics with those for the *E* and *Z* isomers of the corresponding benzimidoylphosphonates [2] (see table).

As follows from the table, the phosphorus and fluorine signals of the *Z* isomers are upfield from those of the *E* isomer. An important spectral dif-

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

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^{31}P, ^{19}F, and ^{13}C NMR spectral parameters (δ, ppm, *J*, Hz) of (*Z*)- and (*E*)-imidoylphosphonates $F_3CP(O)(OAlk)_2{=}NCH_2R$ **I**

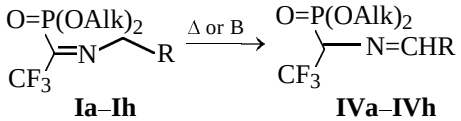
Parameter	Izomer	**Ia**	**Ib**	**Ic**	**Id**	**Ie**	**Ig**
Z/*E*		10	7	6	9	10	7
δ_P	*Z*	–4.4	–6.0	–4.0	–2.6	–4.5	–6.8
	E	2.2	0.9	2.3	3.4	4.4	–1.1
$\delta(CF_3C{=})$ ($^3J_{FP}$)	*Z*	–	–69.5 (<1)	–69.6 (<1)	–69.8 (<1)	–70.1 (<1)	–69.7 (<1)
	E	–	–63.8 (8)	–63.3 (8)	–64.0 (8)	–65.0	–65.0
δ(C=N) ($^1J_{CP}$)	*Z*	–	155.6 (159)	–	154.6 (157)	–	–
	E	–	156.4 (236)	–	–	–	–

ference of the *Z* and *E* isomers is the value of the fluorine–phosphorus coupling constant of the trifluoromethyl group at the C=N bond in the ^{19}F and ^{31}P NMR spectra ($^3J_{PF}$ < 1 and 8 Hz, respectively), as well as the value of the imidoyl carbon–phosphorus coupling constant in the ^{13}C NMR spectra ($^1J_{PC}$ 157–159 and 236 Hz, respectively). The revealed spectral criteria can be used for assignment of isomer signals in related structures.

It is important to note that trifluoroacetimidoylphosphonates exist mainly in the *Z* form [*Z*/*E* ratio (6–10) : 1], while related benzimidoylphosphonates prefer the *E* form [2]. We suggest that this difference is primarily connected with a stronger steric demand of the trifluoromethyl group (cf. [6]).

The regular alteration of the electronic properties of N-substituents in imidoylphosphonates **I** (the σ_I constants are given in Scheme 2 and imidoyl chlorides **II** enables us to trace their effect on the reactivity of compounds **II** toward phosphites (Scheme 1), as well as on the ability of imidoylphosphonates **I** to 1,3-H transfer (Scheme 2). It was established that the reactivity of imidoyl chlorides **II** (**IIb** < **IIa** < **IIc** < **IId**), as well as the tendency for proton transfer in imidoylphosphonates **I** enhances with enhancing electron-acceptor power of substituents R (Me < H < CH_2OMe < CF_3).

Scheme 2.



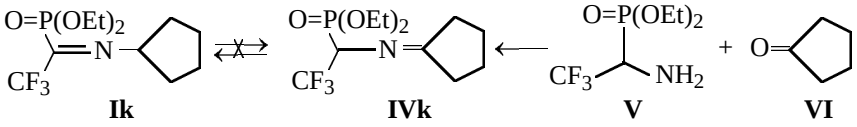
Ia–**Ih** **IVa**–**IVh**

R	Me	H	CH_2OMe	Ph	CF_3
σ_I	–0.05	0	0.1	0.10	0.42

The weakly electron-donor methyl group instead of hydrogen in *N*-methylimidoylphosphonates **Ia** and **Ib** (compound **Ic**) hinders proton transfer, while the electron-acceptor CH_2OMe and CF_3 substituents (compounds **Id, Ie**, and **Ig**) favor this process. Hence, compounds **Ia** and **Ib** in the absence of bases undergo proton transfer neither at room temperature nor on heating to 150°C. Higher temperatures destroy the compounds. Compounds **Id, Ie,** and **Ig** slowly isomerize in boiling toluene. A special group is formed by *N*-benzylimidoylphosphonates **If** and **Ih**. These compounds completely isomerize on heating or distillation, which provides a synthetic approach to α-(benzylideneamino)trifluoroethylphosphonates **IVf** and **IVh** [1, 4]. Comparison of compounds **Ie, Ig** and **If, Ih** is the most illustrative. Despite the fact that CF_3 is a much stronger than phenyl, compounds **If** and **Ih** isomerizes much more easily than **Ie** and **Ig**. Here, evidently, 1,3-H transfer is favored by the formation of the favorable *N*-benzylidene structure in compounds **IVe** and **IVh** [1, 4, 7, 8]. Unlike *N*-benzyltrifluoroacetimidoylphosphonates **If** and **Ih**, compounds **Ia**–**Ie, Ig, Ii,** and **Ij** in the absense of bases either do not izomerize at all or isomerize partially with attendant side processes. At the same time, in the presence of bases (NEt_3, diazabicyclooctane), both *N*-methyl- (**Ia, Ib**) and *N*-CH_2R-imidoylphosphonates (**Ic**–**Ie** and **Ig**) even at room temperature undergo irreversible 1,3-H shift to form alkylideneaminotrifluoroethylphosphonates **IVa**–**IVe** and **IVg**. The effect of substituents R on the rate of the base-catalyzed isometization is the same as in the absence of bases (Me < H < CH_2OMe < CF_3). Hence, in the presence of Et_3N, compounds **Ia** and **Ib** (R = H) isomerize completely at room temperature within 3 h, while the degree of isomerization of imidoylphosphonate **Ic** (R = Me) is only 45%, and the process completes within 15 h. The proton at the *N*-methine carbon atom in imidoylphosphonates is less mobile than in the *N*-methyl or *N*-methylene analogs. As we showed previously [4, 5], *N*-α-phenylethyltrifluoroacetylimidoylphosphonates **Ii** and **Ij** undergo isomerization when heated in the presence of bases (Et_3N, diaza-

bicyclooctane, diazabicycloundecene). The proton transfer is irreversible and stereoselective, which allows preparation of enantiomerically enriched phosphorus analogs of trifluoroalanine [1, 5]. Analogous results with these compounds were later obtained by Xiao *et al.* [9]. At the same time, imidoylphosphonate **Ik** that has a cyclic substituent on nitrogen fails to isomerize even in the presence of nitrogenous bases (Et_3N, 120°C, 2.5 h). It was shown that imidoylphosphonate **Ik** and its independently obtained prototropic isomer **IVk** (Scheme 3) do not interconvert under the same conditions.

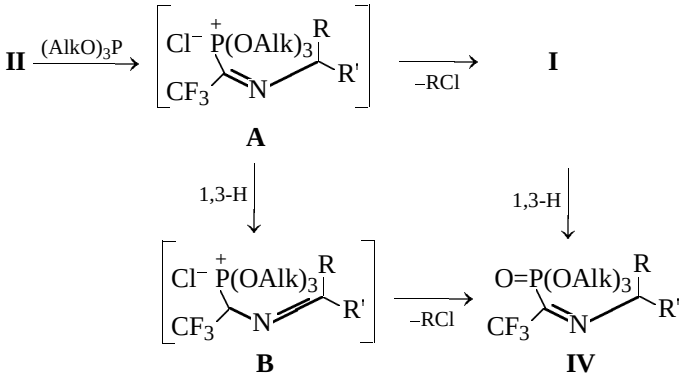
Scheme 3.



Ik **IVk** **V** **VI**

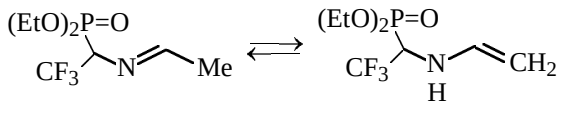
The reactions of imidoyl chlorides **IIc** and **IId** with phosphites involve partial proton transfer just under the reaction conditions (Schemes 1 and 2) to form mixtures of isomers: **IVd**:**Id** (1:10) and **IVe, IVg**:**Id, Ig** (5:1). At the same time, when these mixtures or imidoylphosphonate **Id** isolated pure are heated further, the isomerization **Id, Ie, Ig** → **IVd, IVe, IVg** scarcely occurs. This result suggests that proton transfer in the reaction of imidoyl chlorides **IIc** and **IId** with phosphites takes place only in quasiphosphonium salt **A** (**A** → **B** → **IV**) (Scheme 4). In this case, the process is favored by the combined effect of the strongly electron-acceptor phosphonium group and substituent R (cf. [1, 2, 10, 11]).

Scheme 4.



Note that methylene- (**IVa, IVb**) and alkylideneaminophosphonates (**IVc**) are unstable compounds. The undergo oligomerization even at room temperature to give a mixture of unidentified products. Phosphonate **IVb** that has the diisopropoxyphosphoryl group instead of the less bulky diethoxyphosphoryl group is more stable, but its attempted distillation, too, gave a mixture of unidentified products. α-Phosphorylated imines **IVe** and **IVg** were purified by distillation, and compound **IVc** was characterized by spectroscopy in a mixture. The lability of ethylideneaminophosphonate **IVc** even at room temperature is connected with imine–enamine tautomerism and subsequent transformations of enamine **VII** (Scheme 5), as well as with the tendency of this compound to hydrolyze to form aminophosphonate **V**.

Scheme 5.



IVc **VII**

2-Methoxyethylideneaminophosphonate **IVd** is more stable at room temperature. It could be prepared

spectrally pure (>90%) by isomerization of imidoylphosphonate **Id** in the presence of catalytic amounts of diazabicyclooctane in benzene, and its structure was confirmed by the of ^{1}H, ^{13}C, and ^{19}F NMR spectra. Attempted distillation of compound **IVg** to obtain an analytically pure sample gave a complex mixture of products. Compounds **IV** hydrolyze even when handled at room temperature to form α-aminotrifluoroethylphosphonate **V**. It is important to note that, in spite of the low stability of alkylideneaminophosphonates **IVa**–**IVe** and **Ig**, the transformation sequence **I** → **IV** → **V** can be used to success for preparing phosphonate **V** without isolation of intermediate imines **IV**. However, to prepare phosphorus analogs of trifluoroalanine by means of prototropic rearrangements, phosphorylation of *N*-benzyl- or *N*-(α-phenylethyl)trifluoroacetimidoyl chlorides holds the greatest promise.

The NMR spectra of prototropic isomers **I** and **IV** are clearly distinguished from one another, which makes it possible to identify these compounds in the reaction mixture. Imidoylphosphonates **Ia**–**If** and **Ig** have an upfield phosphorus signal (δ_P 6.8–4.4 ppm), and it suffers a considerable downfield shift when they convert into corresponding **IV** (δ_P 7.9–14.1 ppm). The signal of the CF_3 group at the imidoyl carbon atom in compounds **I** (*Z* isomers: δ_F –69.5 to –70.1 ppm, $^{3}J_{PF}$ < 1 Hz; *E* isomers: δ_P –63.3 to –65.0 ppm and $^{3}J_{PF}$ 8 Hz) transfoms into a triplet in isomers **IV** (δ_F –67.9 to –68.5 ppm, $^{3}J_{FP} = {}^{3}J_{FH}$ 7–8 Hz). The location and coupling constants of carbon atoms bound with phosphorus, too, are much different for imidoylphosphonates **I** (δ_C 154–156 ppm, d.q, $^{1}J_{CP}$ 157–236 Hz, $^{2}J_{CF}$ 35–36 Hz) and phosphorylated imines **IV** (δ_C 68.3–70 ppm, d.q, $^{1}J_{CP}$ 146–148 Hz, $^{2}J_{CF}$ 30 Hz) and confirm the structure of these compounds.

EXPERIMENTAL

The ^{1}H, ^{19}F, ^{31}P, and ^{13}C NMR spectra were recorded on a Varian VXR-300 spectrometer at 299.95, 282.20, 121.42, and 75.43 MHz, respectively. The chemical shifts were measured against internal TMS (^{1}H, ^{13}C) and $CFCl_3$ (^{19}F) and external 85% phosphoric acid (^{31}P).

Trifluoroacetamides III *(general procedure).* Equimolar amounts of ethyl trifluoroacetate and corresponding amine were mixed with cooling in ether (with **IIIc, IIId, and IIIe**) or in methanol (with **IIIb**). After a day [with **IIId**, 7 days], the solvent was evaporated to leave trifluoroacetamide **III**.

***N*-Ethyltrifluoroacetamide (IIIb).** Yield 84%, low-melting crystals {published data: mp 14–15°C [12]}. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.24 t (3H, Me, $^{3}J_{HH}$ 7.2 Hz), 3.41 q (2H, CH_2, $^{3}J_{HH}$ 7.2 Hz), 3.41 q (2H, CH_2, $^{3}J_{HH}$ 7.2 Hz), 6.70 br.s (1H, NH). ^{19}F NMR spectrum ($CDCl_3$): δ_F –76.63 ppm.

***N*-(2-Methoxyethyl)trifluoroacetamide (IIIc)**. Yield 100%, oil. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.39 s (3H, OMe), 3.54 m (4H, CH_2CH_2), 6.86 br.s (1H, NH). ^{19}F NMR spectrum ($CDCl_3$): δ_F –76.0 ppm. Found, %: N 8.35. $C_5H_8F_3NO_2$. Calculated, %: N 8.19.

***N*-(2,2,2-Trifluoroethyl)trifluoroacetatmide (IIId)**. Yield 85%, mp 53-54°C {published data mp 53–54°C [13]}. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.02 m (2H, CH_2, $^{3}J_{HF}$ 8.5 Hz), 6.77 br.s (1H, NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –76.0 s (3F, CF_3CO), –72.4 t (3F, CF_3CH_2, $^{3}J_{HF}$ 8.5 Hz).

***N*-Cyclopentyltrifluoroacetamide (IIIf)**. Yield 100%, mp 71–72°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.4–2.2 m (8H, CH_2), 4.25 m (1H, CH), 6.23 br.s (1H, NH). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –77.0. Found, %: N 7.60. $C_7H_{10}F_3NO$. Calculated, %: N 7.73.

Imidoyl chlorides II *(general procedure).* A mixture of amide **III** with a 10% excess of trichloro(*o*-phenylenedioxy)phosphorane or phosphorus pentachloride (with **IIb**) was refluxed until gaseous products no longer evolved, at 100–130°C with **IId**, 140–150°C with **IIc**, and 180–190°C with **IIf**. Imidoyl chloride was distilled off and then fractionated at atmosperic pressure. Imidoyl chlorides **IIc**–**IIf** were contaminated with $POCl_3$ even after several distillations and were not isolated analytically pure.

***N*-Ethyltrifluoroacetimidoyl chloride (IIb)**. Yield 71%, bp 50–54°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.32 t (3H. Me, $^{3}J_{HH}$ 7.5 Hz), 3.69 q.q (2H, CH_2, $^{3}J_{HH}$ 7,5 Hz, $^{5}J_{HF}$ 1.2 Hz). ^{19}F NMR spectrum ($CDCl_3$): δ_F –72.18 ppm.

***N*-(2-Methoxyethyl)trifluoroacetimidoyl chloride (IIc)**. Yield 63%, bp 130–136°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.40 s (3H, OMe), 3.71 m (2H, CH_2), 3.81 m (2H, CH_2). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 53.4 (CH_2N), 58.9 (OMe), 7.05 (CH_2O), 116.4 q (CFd3, $^{1}J_{CF}$ 277 Hz), 133.5 q (C=N, $^{2}J_{CF}$ 42.5 Hz). ^{19}F NMR spectrum ($CDCl_3$): δ_F –72.06 ppm.

***N*-(2,2,2-Trifluoroethyl)trifluoroacetimidoyl chloride (IId)**. Yield 58%, bp 72–73°C {published data: bp 73°C [14]}. ^{1}N NMR spectrum ($CDCl_3$), δ, ppm: 4.1 q.q (CH_2, $^{3}J_{HF}$ 1.2 Hz). ^{19}F NMR spectrum, δ_F, ppm: –72.25 (3F, CF_3C=N), –71.36 t (3F, $CF_3 \cdot CH_2$, $^{3}J_{HF}$ 8.5 Hz).

***N*-Cyclopentyltrifluoroacetimidoyl chloride (IIe)**. Yield 88%, bp 135–140°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.6–2.0 m (8H, CH_2), 4.20 m (1H, CH). ^{19}F NMR spectrum ($CDCl_3$): δ_F –71.4 ppm.

Diisopropyl *N*-methyltrifluoroacetimidoylphosphonate (Ib). A solution of 0.023 mol of imidoylchloride **IIa** and 0.023 mol of triisopropyl phosphite in 7 ml of toluene was heated in a sealed ampule at 120–130°C for 8 h. The solvent was evaporated, and the residue was distilled in a vacuum. Imidoylphosphonate **Ib** was obtained as a mixture of geometric isomers (*Z*/*E* ~7:1), yield 38%, bp 91–92°C (20 mm Hg), n_D^{20} 1.4036. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.36 d (6H, CH*Me*, $^2J_{HH}$ 6 Hz), 1.40 d (6H, CH*Me*, $^3J_{HH}$ 6 Hz), 3.73 d.q [NMe (*E*), $^4J_{HP}$ 4.2 Hz, $^5J_{HF}$ 2.5 Hz], 3.88 d.q [NMe (*Z*), $^5J_{HF}$ ~ $^4J_{HP}$ 1.8 Hz), 4.6 m [C*H*Me (*E*)], 4.8 m [C*H*Me (*Z*)]. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 23.1 and 23.4 d [*C*H_3C (*Z*), $^3J_{CP}$ 4 Hz], 23.6 and 23.9 d [*C*HH_3C (*Z*), $^3J_{CP}$ (*Z*), $^3J_{CP}$ 3 Hz], 42.6 d.q [CH_3N (*E*), *J* 19.5 and 14.5 Hz], 43.6 d.q [CH_3N (*Z*), *J* 23 and 14 Hz], 71.5 and 71.8 d [OCH (*E*), $^2J_{CP}$ 5.5 Hz], 72.8 and 73.1 d [OCH (*Z*), $^2J_{CP}$ 6.5 Hz], 116.0 q.d [CF_3 (*E*), $^1J_{CF}$ 291, $^2J_{CP}$ 50 Hz), 119.0 q.d [CF_3 (*Z*), $^1J_{CF}$ 279, $^2J_{CP}$ 49.6 Hz], 155.6 d.q [C=N (*Z*), $^1J_{CP}$ 159, $^2J_{CF}$ 35.6 Hz], 156.4 d.q [C=N (*E*), $^1J_{CP}$ 236, $^2J_{CF}$ 30 Hz]. ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –69.5 s (*Z*), –63.8 d.q ($^3J_{FP}$ 8, $^4J_{FH}$ 2.2 Hz) (*E*). ^{31}P–{H} NMR spectrum ($CDCl_3$) δ_P, ppm: –6.0 s (*Z*), 0.9 q ($^3J_{PF}$ 8 Hz) (*E*). Found, %: N 5.01; P 12.08. $C_9H_{17}F_3NO_3P$. Calculated, %: N 5.09; P 11.25.

According to the ^{31}P NMR spectrum, imidoylphosphonate **Ib** in triethylamine solution at room temperature within 3 h completely converts to phosphonate **IVb**, δ_P 10.5 ppm.

Diethyl *N*-ethyltrifluoroacetimidoylphosphonate (Ic). A solution of 0.02 mol of imidoyl chloride **IIg** and 0.03 mol of triethyl phosphite in 4 ml of anhydrous toluene was heated in a sealed ampule at 120°C. According to ^{19}F NMR data, the conversion of the imidoyl chloride was 60%. The ampule was heated for an additional 5 h. The solvent was evaporated, and the residue was distilled in a vacuum. Imidoylphosphonate **Ic** was obtained as a mixture of geometric isomers (*Z*/*E* ~6:1), yield 46%, bp 50°C (0.06 mm Hg), n_D^{20} 1.4043. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.37 m (9H, Me), 4.05–4.35 m (6H, OCH_2 + NCH_2). ^{19}F NMR spectrum, δ_F, ppm: –69.6 (*Z*), –63.3, $^3J_{PF}$ 8 Hz (*E*). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: –4.0 (*Z*), 2.3 (*E*). Found, %: N 4.95. $C_8H_{15}F_3NO_3P$. Calculated, %: N 5.36.

In triethylamine solution at 20°C, compound **Ic** isomerized by 45% within 3 h and completely isomerized into diethyl [1-(ethylideneamino)-2,2,2-trifluoroethyl]phosphonate (**IVc**) within 15 h. The ^{1}H NMR spectrum in $CDCl_3$ contains a CH=N proton signal at 7.9 ppm, d.q, $^3J_{HH}$ ~ $^4J_{HP}$ 4.4 Hz. ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –68.5 t, $^3J_{FH}$ ~ $^2J_{FP}$ 8.2 Hz. ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 13.9. Vacuum distillation gave a mixture of compounds. Its ^{19}F and ^{31}P NMR spectra contained signals of imine **IVc**, enamine **VIII**, δ_F –68.4 and δ_P 13.1 ppm, and aminophosphonate **V** [15], δ_F –71.9 and δ_P 16.8 ppm.

Diethyl *N*-(2-methoxyethyl)trifluoroacetimidoylphosphonate (Id). A solution of 0.01 mol of imidoyl chloride **IIb** and 0.012 mol of triethyl phosphite in 3 ml of anhydrous toluene was refluxed for 5 h. The solvent was evaporated, and the product was distilled in a vacuum. Imidoylphosphonate **Ib** was obtained as a mixture of geometric isomers (*Z*/*E* ~9:1), yield 65%, bp 57–59°C (0.04 mm), n_D^{20} 1.4127. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.38 t [6H, *Me*CH_2 (*Z*), $^3J_{HH}$ 7.5 Hz], 3.39 s [OMe (*Z*)], 3.38 s [OMe (*E*)], 3.76 t [2H, CH_2OC (*Z*), $^3J_{HH}$ 5.4 Hz], 4.3 m (6H, CH_2OP + CH_2N). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm (*Z* isomer): 16.1 d (*Me*CH_2, $^3J_{CP}$ 5.7 Hz), 55.1 d (CH_2N, $^3J_{CP}$ 14 Hz), 58.9 (MeO), 63.6 d (CH_2OP, $^2J_{CP}$ 6.2 Hz), 71.6 (*C*H_2OC), 119.0 q.d (CF_3, $^1J_{CF}$ 281, $^3J_{CP}$ 49 Hz), 154.6 d.q (C=N, $^1J_{CP}$ 157, $^2J_{CP}$ 35 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –69.8 (*Z*), –64.0 $^3J_{FP}$ 8 Hz (*E*). ^{31}P NMR spectrum ($CDCl_3$), δ, ppm: –2.6 (*Z*), 3.4 (*E*). Found, %: N 5.36; P 11.10. $C_9H_{17}F_3NO_4P$. Calculated, %: N 4.81; P 10.64.

Isomerization of trifluoroacetimidoylphosphonate (Id) under the action of bases. *a*. Compound **Id** in triethylamine solution at room temperature isomerizes into phosphonate **IVd** within 5 h; δ_F –67.89 and δ_P 14.1 ppm.

b. To a solution of imidoylphosphonate **Id** in C_6D_6, a catalytic amount of diazabicyclooctane was added. After a day, the solution contained prototropic isomer **IVd** exclusively. ^{1}H NMR spectrum (C_6D_6), δ, ppm: 1.01 t (3H, *Me*CH_2, $^3J_{HH}$ 7 Hz), 1.02 t (3H, *Me*CH_2, $^3J_{HH}$ 6.5 Hz), 3.04 s (3H, OMe), 3.77 d (1H, CH_A·OMe, $^3J_{HH}$ 3.9 Hz), 3.78 d (1H, CH_BOMe, $^3J_{HH}$ 3.9 Hz), 3.88 m (1H, $CHCF_3$, $^3J_{HF}$ 8, $^4J_{HH}$ ~4, $^2J_{HP}$ 6 Hz), 3.9–4.1 m (4H, CH_2OP), 7.54 d.t (1H, CH=N, $^3J_{HH}$ ~ $^4J_{HNCH}$ ~4.2 Hz). The nonequivalence of the methylene protons of the CH_AH_BOMe group is caused by their diastereotopicity. ^{13}C NMR spectrum (C_6D_6), δ, ppm: 16.2 d (*Me*CH_2), 58.4 s (MeO), 63.3 d (CH_2OP, $^2J_{PC}$ 6.4 Hz), 63.7 d (CH_2OP, $^2J_{CP}$ 6.1 Hz), 70.0 d.q (CHP, $^1J_{CP}$ 149, $^2J_{CF}$ 29.5 Hz), 73.8 d (=CH*C*H_2, $^4J_{CP}$ 3 Hz), 124.2 q.d (CF_3, $^1J_{CF}$ 280, $^2J_{CP}$ 2 Hz), 172.2 d (C=N, $^3J_{PC}$ 11 Hz).

Diethyl *N*-cyclopentyltrifluoroacetimidoylphosphonate (Ik). A mixture of 0.01 mol of imidoyl chloride **IIf** and 0.012 mol of triethyl phosphite was refluxed for 3 h at 145–150°C. Vacuum distillation gave phosphonate **Ik**, yield 34%, bp 73–75°C (0.05 mm Hg), n_D^{20} 1.4630. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.38 t (6H, Me, $^3J_{HH}$ 6.9 Hz), 1.6–2.0 m (8H, CH_2), 4.2 m (4H, CH_2O), 4.8 m (1H, CH). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: –69.6 s. ^{31}P NMR spectrum ($CDCl_3$): δ_P –2.9 ppm. Found, %: N 4.68; P 10.54. $C_{11}H_{19}F_3NO_3P$. Calculated, %: N 4.65; P 10.28.

Diethyl [1-(2,2,2-trifluoroethylideneamino)-2,2,2-trifluoroethyl]phosphonate (IVe). A solution of 0.003 mol of imidoyl chloride **IId** and 0.003 mol of triethyl phosphite in 3 ml of anhydrous toluene was heated in the sealed ampule at 120°C for 2.5 h. According to ^{19}F and ^{31}P NMR data, the reaction mixture contains a mixture of prototropic isomers **IVe**/**Ie** (~5 : 1). Imidoylphosphonate **Id**: δ_F, ppm: –72.2 t (CF_3CH_2); –70.1 [CF_3C=N (*Z*)]; –65.0 [CF_3C=N (*E*)]; δ_P, ppm: –4.5 (*Z*), 4.4 (*E*), *Z*/*E* 10 : 1. Triethylamine, 5 ml, was added. After 30 min, signals of imidoylphosphonate completely disappeared. The resulting solution was filtered, evaporated, and the residue was distilled in a vacuum. Yield of phosphonate **IVd** 33%, bp 76°C (6 mm Hg), n_D^{20} 1.3758. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.38 m (6H, Me), 4.22 m (5H, CH_2O + CHP), 7.87 d.q (1H, CH=, $^3J_{HF}$ ~ $^4J_{HP}$ ~3.5 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –72.43 br.s (3F, CF_3CH=), –68.25 t (3F, CF_3CHP, $^3J_{FH}$ ~ $^4J_{FP}$ ~7.6 Hz). ^{31}P NMR spectrum, δ_P, ppm: 9.8. Found.%: P 9.88. $C_8H_{12}F_6NO_3P$. Calculated, %: P 9.83.

Diisopropyl [1-(2,2,2-trifluoroethylideneamino)-2,2,2-trifluoroethyl]phosphonate (IVg). A solution of 0.007 mol of imidoyl chloride **IId** and 0.007 mol of triisopropyl phosphite in 6 ml of anhydrous toluene was heated in a sealed ampule at 120°C for 4 h. According to ^{1}F and ^{31}P NMR data, the ratio of prototropic isomers **IVg** and **Ig** was ~5 : 1. Imidoylphosphonate **Ig**: δ_F, ppm: –72.2 t (CF_3CH_2); –69.7 [CF_3C=N (*Z*)], –65.0 [CF_3C=N (*E*)]; δ_P –6.8 ppm (*Z*), –1.1 ppm (*E*), *Z*/*E* ~7 : 1. Triethylamine, 0.2 g, was added. After a day, the solvent was evaporated, and the residue was distilled in a vacuum. Yield 33%, bp 87–90°C (6 mm Hg), n_D^{20} 1.3810. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.34 m (12H, Me), 4.25 d.q (1H, CHP, $^2J_{HP}$ 18.8, $^3J_{HF}$ 8.2 Hz), 4.83 m (2H, CHO), 7.86 d.q (1H, CH=, $^3J_{HF}$ ~ $^4J_{HP}$ ~4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 23.5 (CH_3, $^3J_{CP}$ 4 Hz), 23.9 (CH_3, $^3J_{CP}$ 5 Hz), 68.3 d.q (CHP, $^1J_{CP}$ 146, $^1J_{CF}$ 30 Hz), 73.7 d (CHO, $^2J_{CP}$ 7 Hz), 74.1 d (CHO, $^2J_{CP}$ 7 Hz), 118.1 q.d (CF_3CO, $^1J_{CF}$ 278, $^2J_{CP}$ 3.5 Hz), 122.5 q.d (*C*F_3CH=, $^1J_{CH}$ 280, $^4J_{CP}$ 7 Hz), 156.7 q.d (C=N, $^2J_{CF}$ 39.5, $^3J_{CP}$ 10.6 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –72.45 br.s (3F, CF_3CH=N); –67.95 t (3F, CF_3CHP, $^3J_{FH}$ ~ $^3J_{PF}$ ~7.8 Hz). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 7.9. Found, %: N 4.09; P 9.56. $C_{10}H_{16}F_6NO_3P$. Calculated, %: N 4.08; P 9.02.

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