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# Protonation and Alkylation of Organophosphorus Compounds with Trifluoromethanesulfonic Acid Derivatives

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**Abstract**—Protonation (alkylation) of triphenylphosphine, triethylphosphite, triphenylphosphine oxide, triethylphosphate, hexamethylphosporamide, and dimethylphosphite with trifluoromethanesulfonic acid, its bisimide, and methyl ester was studied and the corresponding $^{1}H$, $^{13}C$, $^{19}F$, $^{31}P$ NMR spectra were analyzed.

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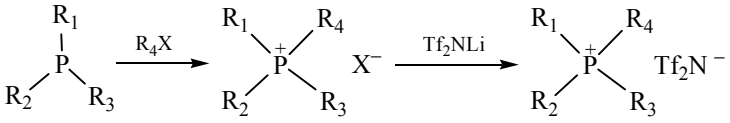
Phosphonium salts of the type $R_4P^+X^-$, in particular, triaryl(alkyl)phosphonium salts, readily prepared by the reaction of triarylphosphines with alkyl halides [1], are widely used in organic synthesis for preparation of olefins (Wittig reaction and its modifications, Wittig–Horner or Horner–Wadsworth–Emmons reaction) [2]. In the recent time, papers appeared describing the synthesis and application of the phosphonium salts [3, 4] and ionic liquids (IL) based on the phosphonium cation $R_4P^+$, the so-called specifically designated ILs [5, 6], including those containing the bis(trifluoromethanesulfonyl)imide anion. Bis(trifluoromethanesulfonyl)-imide $(CF_3SO_2)_2NH$ (triflimide) attracts the attention of researchers by its high acidity: its p$K_a$ in water is 1.7 [7], and the gas phase acidity is 291.8 kcal mol$^{-1}$, which is by 7.7 kcal mol$^{-1}$ larger than that of the acid $CF_3SO_3H$ itself [8]. Its lithium salt $(CF_3SO_2)_2NLi$ is used in electrolytes for batteries [9–12], whereas the salts of other metals [13] are used as water-resistant Lewis acids in reactions of alkylation, acylation, nucleophilic substitution, and Diels–Alder cycloaddition [14–19]. Lithium salt $(CF_3SO_2)_2NLi$ is also used in a two-step synthesis of ILs, which includes quaterniza-tion of the nitrogen or phosphorus atom followed by anionic exchange [20], as shown in scheme (1) for the phosphorus derivatives.




(1)

Tf = $CF_3SO_2$.

Ionic liquids possessing anion $(CF_3SO_2)_2N^-$ or its analogs usually have the lowest melting points and viscosity, and, besides, they are hydrophobic and thermally and electrochemically stable [21–25], and they found a wide application [26].

At the same time, there are no data in the literature on the reactions of triflimide with phosphines, phosphine oxides, phosphites, phosphates, and other phosphorus-containing nucleophiles. The closest study is the paper of Hiemisch et al. [27], who investigated the following reactions:

$$Ph_3P + HN(SO_2F)_2 \rightarrow Ph_3P^+H[(FSO_2)_2N^-], \quad (2)$$

$$Ph_3PO + HN(SO_2F)_2 \rightarrow Ph_3PO{\cdot}HN(SO_2F)_2. \quad (3)$$

The structure of the former salt was proved by XRD analysis, whereas the structure of the latter product was not established unambiguously. Two alternatives were considered: the hydrophosphonium salt $[Ph_3POH]^+[(FSO_2)_2N]^-$ by analogy with hydroxytriphenylphosphonium chloride $[Ph_3POH]^+Cl^-$ [28], or the H-complex $Ph_3P{=}O\cdots HN(SO_2F)_2$ similar to the complex $Ph_3P{=}O\cdots HN(SO_2Me)_2$ [29].

The reaction of magic acid $HSO_3F$–$SbF_5$ (1:1) with $Ph_3P$, $Ph_3P$=O, and polyfluoroaromatic phosphines and their derivatives $C_6F_5PX_2$ (X = H, Me, Ph, $C_6F_5$, Cl, F, NCS, CN, OMe, $NEt_2$) was shown to lead to stable phosphonium ions $C_6F_5P^+HX$; in the latter case the protonation occurs at the nitrogen atom $C_6F_5(NEt_2)\cdot(N^+HEt_2)$ [30].

It should be mentioned that this result is specific for polyfluorinated phosphoramides since phosphines are stronger nucleophiles than the corresponding amines [31]. For example, the quaternization of dimethylaminodimethylphosphine $(CH_3)_2PN(CH_3)_2$ with methyl iodide takes place at the phosphorus atom as proved by the formation of dimethylamine at the hydrolysis of the salt [32]. Apparently, the protonation of the nitrogen atom in $C_6F_5P(NEt_2)_2$ [30] is due to a strong electron-withdrawing effect of the pentafluorophenyl group.

In continuation of our studies of the triflic, triflamide, and triflimide salts and ionic liquids [33, 34], we have now investigated the reaction of some phosphorus-containing nucleophiles [$Ph_3P$ (**I**), $(EtO)_3P$ (**II**), $Ph_3P$=O (**III**), $(EtO)_3P$=O (**IV**), $(Me_2N)_3P$=O (**V**), $(MeO)_2P(O)H$ (**VI**)], with truifluoromethanesulfonic acid $CF_3SO_3H$ (**VII**) and its imide $(CF_3SO_2)_2NH$ (**VIII**), *N*-(phenyl)trifluoromethanesulfonylimide $(CF_3SO_2)_2NPh$ (**IX**), and methyl ester $CF_3SO_2OMe$ (**X**). In a number of cases the products of the reactions are readily hydrolized with the formation of unseparable side-products, therefore, not for all products the analytically pure samples could be obtained.

The reaction of triphenylphosphine **I** with strong acids **VII** and **VIII** at room temperature in methylene chloride or benzene affords the corresponding salts **XI, XII** in quantitative yield.

$$YH + PPh_3 \rightarrow Ph_3P^+–H\ Y^-, \quad (4)$$
$$\textbf{XI, XII}$$

Y = TfO (**XI**), $Tf_2N$ (**XII**); Tf = $CF_3SO_2$.

The structure of the formed phosphonium salts **XI, XII** is confirmed by the presence in their $^1H$ and $^{31}P$ NMR spectra of the doublets of the PH group with characteristic coupling constants $J_{PH}$ 531 Hz (**XI**) and 522 Hz (**XII**) (cf. [35]). The salt formation results in a shift of the singlet of aromatic protons in the $^1H$ NMR spectrum at 7.3 ppm in phosphine **I** to 7.6–7.8 ppm and its splitting to multiplets of the *o*-, *m*- and *p*-protons. In the $^{13}C$ NMR spectrum, the signal of the $C_p$ atom moves downfield by 7–8 ppm, whereas the signal of the $C_i$ atom moves upfield by more than 20 ppm, and the $^1J_{PC}$ coupling constant, in accordance with the literature data [36], increases from ~10 to ~80 Hz.

The presence of anion $Tf_2N^-$ in salt **XII** is also corroborated by the IR spectrum, which is in agreement with the literature data on a low-frequency shift of the $\nu_{as}(SO_2)$ band in the anions of bisimides relative to the neutral molecules from ~1440 $cm^{-1}$ to 1300–1350 $cm^{-1}$ [7, 37–39].

We tried to prepare the tetraphenylphosphonium salt of triflimide by the reaction of triphenylphosphine **I** with *N*-phenyltriflimide **IX**, but the reaction did not occur even at long reflux in benzene (14 h), or with microwave activation.

$$Tf_2NPh + PPh_3 \rightarrow Ph_3P^+–Ph\ Tf_2N^-. \quad (5)$$

Triphenylphosphine is known to be alkylated with esters of sulfonic acids at high temperatures (up to 170°C) with the formation of alkyltriaryl- and tetraalkylphosphonium sulfonates [40]. A higher nucleofugacity of trifluoromethanesulfonyl group as compared to the residues of other sulfonic acids allowed to perform the reaction of phosphine **I** with ester **X** under much milder conditions, in ~3 h at room temperature in methylene chloride in quantitative yield.

$$Ph_3P + TfOMe \rightarrow Ph_3P^+–Me\ TfO^-. \quad (6)$$
$$\textbf{XIII}$$

The structure of salt **XIII** is proved by the shift of the signal of the methyl protons in the $^1H$ NMR spectrum by 1.3 ppm relative to ester **X** and by its splitting with the coupling constant $^2J_{PH}$ 13Hz, as well as by the presence of a doublet of the methyl carbon in the $^{13}C$ NMR spectrum with the coupling constant $^1J_{PC}$ 59 Hz and the coincidence of the aromatic part of the $^{13}C$ NMR spectrum of salt **XIII** with that of salts **XI, XII**.

Similarly, the reaction of triethylphosphite **II** with acids **VII** and **VIII** gives salts **XIV** and **XV**:

$$YH + P(OEt)_3 \rightarrow (EtO)_3P^+–H\ Y^-, \quad (7)$$
$$\textbf{XIV, XV}$$

Y = TfO (**XIV**), $Tf_2N$ (**XV**).

The $^1H$ and $^{13}C$ NMR spectra of salts **XIV, XV** are practically identical, in the proton spectra the doublets of PH with the coupling constants $^1J_{PH}$ 745 Hz (**XIV**) and 729 Hz (**XV**) are observed, which coincide with those in the $^{31}P$ NMR spectra (cf. with the NMR data

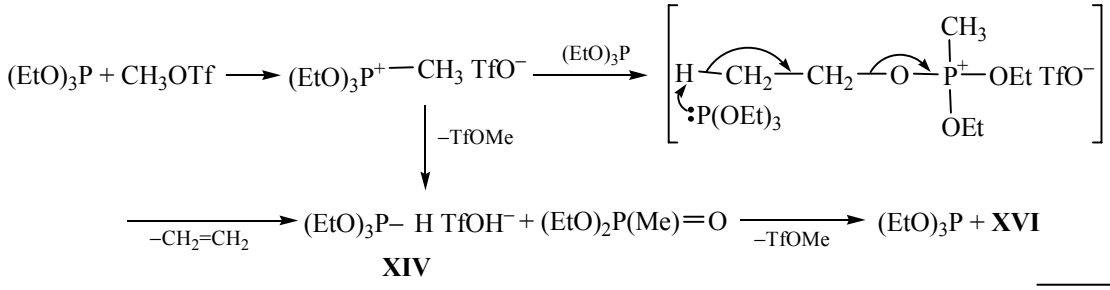
for salt $(EtO)_3PH^+FSO_3^-$ in $FSO_3H$ solution at –60°C [41]).

Similar to triphenylphosphine, the triethylphosphite does not react with compound **IX** even at long reflux in benzene.

Salts **XIV, XV** are hydrolyzed at standing with the formation of ethanol and diethylphosphite **XVI** according to scheme (8), as shown by the appearance of the corresponding signals in the $^1H$, $^{13}C$, and $^{31}P$ NMR spectra.

$$(EtO)_3PH^+Y^- \xrightarrow[-EtOH,\ -HY]{H_2O} [(EtO)_2P(OH)] \rightarrow (EtO)_2P(O)H \quad \textbf{XVI} \qquad (8)$$

Triethylphosphite reacts with ester **X** with the formation of several products, which we failed to separate. The major product, according to $^1H$ and $^{31}P$ NMR spectra, is diethylphosphite **XVI**. Taking into account the literature data [42, 43], the following scheme of transformations may be suggested:




(9)

The formation of salt $(EtO)_3P^+Me\ TfO^-$ is proved by the presence of a doublet of multiplets of the $PCH_3$ methyl group in the $^1H$ NMR spectrum with the coupling constant $^2J_{PCH}$ 12.1 Hz, and the signal in the $^{31}P$ NMR spectrum at 50.4 ppm, which is characteristic of such salts [43]. The formation of esters **X** and TfOEt is indicated by the presence of a signal at –75 ppm in the $^{19}F$ NMR spectrum, which coincides with the $^{19}F$ NMR signal of compound **X**.

The reaction of triphenylphosphine oxide **III** with compounds **VII, VIII**, and **X** gives rise to salts **XVII–XIX**.

$$YR + Ph_3P{=}O \rightarrow Ph_3P^+{-}OR\ Y^-, \qquad (10)$$

Y = TfO, R = H (**XVII**); Y = $Tf_2N$, R = H (**XVIII**); Y = TfO, R = Me (**XIX**).

Salts **XVII** and **XIX** are syrup-like liquids, and salt **XVIII** is a crystalline compound with mp 78°C. In the $^1H$ NMR spectra of all salts the signal of the $H_p$ protons is shifted relative to the starting compound **III** by ~0.3 ppm and becomes the most downfield aromatic signal. In the $^{13}C$ NMR spectra the signal of $C_p$ is shifted downfield by ~3 ppm, and the signal of $C_i$ is shifted upfield by ~10 ppm. The methyl group in IL **XIX** is split into a doublet with the coupling constants $J_{PH}$ = 12.1 Hz in the $^1H$ NMR spectrum and with $J_{PC}$ = 7.7 Hz in the $^{13}C$ NMR spectrum.

Similar to triphenylphosphine oxide **III**, triethylphosphate **IV** reacts with trifluoromethanesulfonic acid **VII**, bis(trifluoromethanesulfonyl)imide **VIII**, and methyl triflate **X**. The reactions with the formation of **XX** and **XXI** proceed smoothly in $CH_2Cl_2$ in high yields at room temperature.

$$YR + (EtO)_3P{=}O \rightarrow (EtO)_3P^+{-}OR\ Y^-, \qquad (11)$$

Y = TfO, R = H (**XX**); Y = $Tf_2N$, R = H (**XXI**); Y = TfO, R = Me (**XXII**).

In the $^1H$ NMR spectra of salts **XX, XXI** the signals of the $CH_2$ and $CH_3$ groups are shifted downfield by 0.5–0.6 ppm relative to the starting ester **IV** and the line shape of the multiplets is changed. For salt **XX**, the signal of the $CH_2$ group is a doublet of doublets of quartets with the coupling constants $^3J_{HH}$, $^3J_{HP}$ and $^5J_{HH}$, and the $CH_3$ group gives rise to a triplet of triplets due to the close small constants $^4J_{HP}$ and $^6J_{HH}$. In ester **IV**, the signal of the $CH_2$ group is a doublet of quartets with close constants $^3J_{HH}$ = 7.1 Hz and $^3J_{HP}$ = 7.6 Hz, and the $CH_3$ group looks like a a doublet of triplets with a small constant $^4J_{HP}$ = 0.8 Hz. The reaction of esters **IV** and **X**, apart from salt **XXII**, gives rise to the products of transalkylation, $(MeO)_2(EtO)_2P^+ \cdot TfO^-$ and $(EtO)_4P^+\ TfO^-$, as proved by the presence of minor doublets of the MeO group in the $^1H$ and $^{13}C$

NMR spectra, as well as the $CH_2$ group in the $^{13}C$ NMR spectrum. The ratio of the salts determined from the intensity of the signals in the $^1H$ NMR spectrum is ~3:1:3.

The reaction of hexamethylphosphortriamide **V** with acid **VII** and imide **VIII** results in a downfield shift of the signals in the $^1H$ and $^{31}P$ NMR spectra by 0.4 and ~9 ppm, respectively. Also, in the $^1H$ NMR spectra downfield signals of OH are present with the ratio of intensities OH : NMe = 1 : 18. These data are indicative of the formation of salts **XXIII, XXIV**:

$$(Me_2N)_3P{=}O + YH \rightarrow (Me_2N)_3P^+{-}OH\ Y^-, \quad (12)$$

Y = TfO (**XXIII**), $Tf_2N$ (**XXIV**).

The presence in the IR spectrum of compound **XXIV** of the band $\nu_{as}(SO_2)$ at 1353 $cm^{-1}$, which belongs to anion $Tf_2N^-$ (see above), proves its salt nature.

The reaction of hexamethylphosphortriamide **V** with ester **X** affords the O-methylation product, tris-(dimethylamino)(methoxy)phosphonium triflate **XXV**. In its $^1H$ and $^{13}C$ NMR spectra, the doublets of the OMe and NMe groups are observed in the ratio of 1:6.

$$(Me_2N)_3P{=}O + CF_3SO_3Me \rightarrow (Me_2N)_3P^+{-}OMe\ CF_3SO_3^-, \quad (13)$$

**XXV**

Dimethylphosphite **VI** reacts with acid **VII** and imide **VIII** to give salts **XXVI, XXVII**:

$$(MeO)_2P(O)H + YH \rightarrow (MeO)_2P^+H{-}OH\ Y^-, \quad (14)$$

Y = TfO (**XXVI**), $Tf_2N$ (**XXVII**).

The $^1H$ NMR spectra of these compounds contain the OH group signal in a very low field (15 ppm for salt **XXVI** and 13 ppm for salt **XXVII**). The signals of the OMe and PH protons are shifted downfield by 0.2 ppm with respect to the starting compound **VI**, and the coupling constant $^1J_{PH}$ increases by 30–40 Hz. In the reaction of dimethylphosphite **VI** with acid **VII** a side reaction of transesterification is observed with the formation of about 10% of methyl triflate **X** and ester MeOPH(O)(OH). This is proved by the presence in the $^{19}F$ NMR spectrum of the reaction product of the signal at –74.3 ppm, in the $^{13}C$ NMR spectrum, of a minor doublet signal at 54.0 ppm with $J_{PC}$ 6 Hz, and in the $^1H$ NMR spectrum, of the singlet of the methyl group at 3.69 ppm from **X** and the doublet at 3.86 ppm with the coupling constant ~12 Hz. For salt **XXVI**, a weak splitting of the OMe signal with the long-range coupling $^4J_{HH}$ = 0.5 Hz is observed. In the $^{13}C$ NMR spectrum the signal of the methoxy group is also shifted downfield by ~2 ppm.

The reaction of compound **VI** with ester **X** does not give the expected trimethoxyphosphonium triflate $(MeO)_3PH^+\ TfO^-$. The NMR spectra of the reaction product are practically identical with the spectra of the starting **VI**, being slightly shifted downfield due to the partial hydrolysis of ester **X** and the acidity of the medium. Apparently, the reversibly formed product $(MeO)_3PH^+\ TfO^-$ easily decomposes in the starting components, and also eliminates methanol, as proved by its formation and condensation in a cooled trap when carrying out the reaction in thoroughly dried methylene chloride.

## EXPERIMENTAL

IR spectra were recorded on a Bruker Vertex 70 instrument in thin film or in KBr. NMR spectra were taken on a Bruker DPX 400 spectrometer at working frequencies 400 ($^1H$), 100 ($^{13}C$), 376 ($^{19}F$), 162 ($^{31}P$) MHz in $CDCl_3$, using the signals of the residual protons of the solvent (for $^1H$), or carbon atoms (for $^{13}C$) as an internal reference, chemical shifts are given relative to TMS ($^1H$, $^{13}C$), $CCl_3F$ ($^{19}F$), $H_3PO_4$ ($^{31}P$).

*N*-Phenyl-bis(trifluoromethanesulfonyl)imide **IX** and methyltrifluoromethanesulfonate **X** were prepared as described earlier in [44] and [45, 46], respectively.

**Triphenylphosphonium trifluoromethanesulfonate (XI)**. To the solution of 0.22 g (1.45 mmol) of acid **VII** in 3 ml of methylene chloride or benzene the solution of 0.38 g (1.45 mmol) of phosphine **I** in 2 ml of the same solvent was added at vigorous stirring, the mixture was stirred for 3 h at room temperature and evaporated to give 0.60 g (100%) of salt **XI** as white crystals with mp 98–99°C. IR spectrum, ν, $cm^{-1}$: 3064, 2405, 1586, 1482, 1441, 1282, 1225, 1152, 1115, 1031, 907, 749, 722, 691, 638, 510, 492. $^1H$ NMR spectrum, δ, ppm: 7.80–7.67 m (15H, Ar), 9.38 d (1H, $J_{PH}$ 530.9 Hz). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 115.62 d ($C_i$, $J_{CP}$ 86.6 Hz), 120.02 q ($CF_3$, $J_{CF}$ 319.1 Hz), 130.52 d ($C_m$, $J_{CP}$ 13.3Hz), 134.01 d ($C_o$, $J_{CP}$ 11.1 Hz), 135.49 d ($C_p$, $J_{CP}$ 2.6 Hz). $^{19}F$ NMR spectrum, $\delta_F$, ppm: –78.23. $^{31}P$ NMR spectrum, $\delta_P$, ppm: 3.89 d (PH, $J_{PH}$ 531.2 Hz). Found, %: C 56.04; H 3.88; F 13.73; P 7.43; S 8.12. $C_{19}H_{16}F_3O_3PS$. Calculated, %: C 55.34; H 3.91; F 13.82; P 7.51; S 7.78. Compounds **XII–XXVII** were obtained similarly.

**Triphenylphosphonium bis(trifluoromethanesulfonyl)-imide (XII)**. Yield 98%, colorless syrup-like liquid. IR spectrum, ν, $cm^{-1}$: 3066, 2426, 1588, 1484, 1442, 1352, 1197, 1136, 1057, 897, 743, 689, 615, 570, 510. $^1H$ NMR spectrum, δ, ppm: 7.82–7.68 m (15H, Ar), 8.94 d (P–H, $J_{PH}$ 521.8 Hz). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 115.75 d ($C_i$, $J_{CP}$ 73.7 Hz), 119.72 q ($CF_3$, $J_{CF}$ 321.5 Hz), 130.48 d ($C_m$, $J_{CP}$ 13.3Hz), 133.78 d ($C_o$, $J_{CP}$ 11.8 Hz), 135.40 s ($C_p$). $^{19}F$ NMR spectrum, $\delta_F$, ppm: –78.78. $^{31}P$ NMR spectrum, $\delta_P$, ppm: 5.28 d (PH, $J_{PH}$ 519.7 Hz). Found, %: C 44.83; H 2.83; N 2.51; S 11.23. $C_{20}H_{16}F_6NO_4PS_2$. Calculated, %: C 44.20; H 2.97; N 2.58; S 11.80.

**Methyltriphenylphosphonium trifluoromethanesulfonate (XIII)**. Yield 100%, white crystals, mp 128°C. IR spectrum, ν, $cm^{-1}$: 3443, 1589, 1486, 1440, 1260, 1152, 1116, 1030, 903, 745, 690, 637, 501. $^1H$ NMR spectrum, δ, ppm: 2.94 d (3H, $CH_3$, $J_{HP}$ 12.6 Hz), 7.81–7.65 m (15H, Ar). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 9.46 d ($CH_3$, $J_{CP}$ 58.2 Hz), 119.72 q ($CF_3$, $J_{CF}$ 321.5 Hz), 118.99 d ($C_i$, $J_{CP}$ 88.5 Hz), 130.48 d ($C_m$, $J_{CP}$ 13.3Hz), 133.08 d ($C_o$, $J_{CP}$ 10.3Hz), 135.19 d ($C_p$, $J_{CP}$ 2.21 Hz). $^{19}F$ NMR spectrum, $\delta_F$, ppm: –77.81. $^{31}P$ NMR spectrum, $\delta_P$, ppm: 24.43. Found, %: C 55.30; H 4.48; F 14.17; P 7.47; S 7.86. $C_{20}H_{18}F_3O_3PS$. Calculated, %: C 56.34; H 4.26; F 13.37; P 7.26; S 7.52.

**Triethoxyphosphonium trifluoromethanesulfonate (XIV)**. Yield 87%, light-brown liquid. IR spectrum, ν, $cm^{-1}$: 2991, 2939, 2917, 2467, 1714, 1249, 1229, 1197, 1181, 1032, 639, 516. $^1H$ NMR spectrum, δ, ppm: 1.39 t (9H, $CH_3$, $J$ 7.0 Hz), 4.28 d.q (6H, $CH_2$, $J_{PH}$ 8.65, $J_{HH}$ 7.23Hz), 6.97 d (1H, $J_{PH}$ 743.0 Hz). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 15.83 d ($CH_3$, $J_{CP}$ 6.2 Hz), 65.1 d ($CH_2$, $J_{CP}$ 6.2 Hz), 119.32 q ($CF_3$, $J_{CF}$ 317.8 Hz). $^{19}F$ NMR spectrum, $\delta_F$, ppm: –78.18. $^{31}P$ NMR spectrum, $\delta_P$, ppm: 9.31 d ($J_{PH}$ 744.6 Hz).

**Triethoxyphosphonium bis(trifluoromethanesulfonyl)imide (XV)**. Yield 82%, light-brown liquid. IR spectrum, ν, $cm^{-1}$: 3243, 2993, 2469, 1443, 1353, 1196, 1139, 1061, 880, 791, 613, 572, 514. $^1H$ NMR spectrum, δ, ppm: 1.40 t (9H, $CH_3$, $J$ 7.1 Hz), 4.22 d.q (6H, $CH_2$, $^3J_{PH}$ 9.1, $^3J_{HH}$ 7.1 Hz), 6.88 d (1H, PH, $^1J_{PH}$ 729.1 Hz). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 15.95 d ($CH_3$, $J_{CP}$ 6.3Hz), 64.13 d ($CH_2$, $J_{CP}$ 5.9 Hz), 119.06 q ($CF_3$, $J_{CF}$ 322.3Hz). $^{19}F$ NMR spectrum, $\delta_F$, ppm: –77.29. $^{31}P$ NMR spectrum, $\delta_P$, ppm: 9.01 d ($J_{PH}$ 725.08 Hz).

**Hydroxytriphenylphosphonium trifluoromethanesulfonate (XVII)**. Yield 100%, syrup-like liquid. IR spectrum, ν, $cm^{-1}$: 3064, 1591, 1440, 1313, 1204, 1188, 1124, 1025, 979, 731, 690, 635, 534. $^1H$ NMR spectrum, δ, ppm: 7.78–7.64 m (15H, Ar), 10.71 s (1H). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 119.57 q ($CF_3$, $J_{CF}$ 318.6 Hz), 122.93 d ($C_i$, $J_{CP}$ 109.1 Hz), 129.70 d ($C_m$, $J_{CP}$ 13.6 Hz), 132.76 d ($C_o$, $J_{CP}$ 11.4 Hz), 135.13 d ($C_p$, $J_{CP}$ 1.8 Hz). $^{19}F$ NMR spectrum, $\delta_F$, ppm: –78.32. $^{31}P$ NMR spectrum, $\delta_P$, ppm: 53.12. Found, %: C 54.60; H 2.97; F 14.18; P 6.58; S 7.13. $C_{19}H_{16}F_3O_4PS$. Calculated, %: C 53.27; H 3.76; F 13.31; P 7.23; S 7.49.

**Hydroxytriphenylphosphonium bis(trifluoromethanesulfonyl)imide (XVIII)**. Yield 88%, white crystals, mp 69°C. IR spectrum, ν, $cm^{-1}$: 3438, 1439, 1356, 1334, 1200, 1142, 1125, 1050, 729, 692, 611, 574, 539. $^1H$ NMR spectrum, δ, ppm: 7.81–7.67 m (15H, Ar), 9.94 s (1H). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 119.16 q ($CF_3$, $J_{CF}$ 320.9 Hz), 122.42 d ($C_i$, $J_{CP}$ 109.1 Hz), 129.83 d ($C_m$, $J_{CP}$ 13.6 Hz), 132.73 d ($C_o$, $J_{CP}$ 11.8 Hz), 135.40 d ($C_p$, $J_{CP}$ 2.2 Hz). $^{19}F$ NMR spectrum, $\delta_F$, ppm: –77.60. $^{31}P$ NMR spectrum, $\delta_P$, ppm: 55.59. Found, %: C 42.73; H 2.86; F 20.48; N 2.70; P 5.18; S 11.75. $C_{20}H_{16}F_6NO_5PS_2$. Calculated, %: C 42.94; H 2.88; F 20.38; N 2.50; P 5.54; S 11.46.

**Methoxytriphenylphosphonium trifluoromethanesulfonate (XIX)**. Yield 100%, light-yellow crystals, mp 37°C. IR spectrum, ν, $cm^{-1}$: 3066, 1440, 1267, 1225, 1162, 1123, 1030, 732, 692, 638, 545, 531. $^1H$ NMR spectrum, δ, ppm: 4.10 d (3H, $CH_3$, $J_{HP}$ 12.1 Hz), 7.88–7.57 m (19.2 H, Ar). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 58.03 d ($CH_3$, $J_{CP}$ 7.7 Hz), 118.29 d ($C_i$, $J_{CP}$ 106.5 Hz), 130.53 d ($C_m$, $J_{CP}$ 13.6 Hz), 133.38 d ($C_o$, $J_{CP}$ 11.9 Hz), 136.45 d ($C_p$, $J_{CP}$ 2.2 Hz). $^{19}F$ NMR spectrum, $\delta_F$, ppm: –78.31. $^{31}P$ NMR spectrum, $\delta_P$, ppm: 65.19.

**Triethoxy(hydroxy)phosphonium trifluoromethanesulfonate (XX)**. Yield 98%, colorless syrup-like liquid. IR spectrum, ν, $cm^{-1}$: 2991, 2939, 2917, 1708, 1313, 1200, 1034, 822, 638, 515. $^1H$ NMR spectrum, δ, ppm: 1.36 t.t (9H, $CH_3$, $^3J_{HH}$ 7.1, $^4J_{PH} = {}^6J_{HH}$ 1.3Hz), 4.20 d.q (6H, $CH_2$, $^3J_{PH}$ 8.1, $^3J_{HH}$ 7.0, $^5J_{HH}$ 1.2 Hz). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 15.68 d ($CH_3$, $J_{CP}$ 6.6 Hz), 66.57 d ($CH_2$, $J_{CP}$ 6.3 Hz), 119.59 q ($CF_3$, $J_{CF}$ 318.1 Hz). $^{19}F$ NMR spectrum, $\delta_F$, ppm: –78.55. $^{31}P$ NMR spectrum, $\delta_P$, ppm: –2.04.

**Triethoxy(hydroxy)phosphonium bis(trifluoromethanesulfonyl)imide (XXI)**. Yield 96%, light yellow liquid. IR spectrum, ν, $cm^{-1}$: 3265, 2993, 1445, 1353, 1195, 1140, 1037, 820, 616, 572, 514. $^1H$ NMR spectrum, δ, ppm: 1.39 t (3H, $CH_3$, $J$ 7.1 Hz), 4.20 q

(9H, $CH_2$, *J* 7.2 Hz), 4.22 q (6H, $CH_2$, *J* 7.5 Hz), 14.41 s (1H). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 15.75 d ($CH_3$, $J_{CP}$ 6.6 Hz), 66.09 d ($CH_2$, $J_{CP}$ 6.3 Hz), 119.36 q ($CF_3$, $J_{CF}$ 321.6 Hz). $^{19}F$ NMR spectrum, $\delta_F$, ppm: –77.96. $^{31}P$ NMR spectrum, $\delta_P$, ppm: – 2.98.

**Triethoxy(methoxy)phosphonium trifluoromethanesulfonate (XXII)** was prepared as a mixture with the products of transalkylation $(MeO)_2(EtO)_2P^+$ $TfO^-$ and $(EtO)_4P^+$ $TfO^-$, total yield 96%, light yellow liquid. IR spectrum, ν, $cm^{-1}$: 2989, 2916, 1447, 1396, 1274, 1225, 1166, 1031, 824, 639, 517. $^1H$ NMR spectrum, δ, ppm: 1.20 t (9H, $CH_3$, *J* 7.3 Hz), 3.63 d (3H, $OCH_3$, *J* 11.3 Hz), 3.99 q (6H, $OCH_2$, *J* 7.3 Hz). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 15.50 d ($CH_3$, $J_{CP}$ 6.3 Hz), 54.23 d ($OCH_3$, $J_{CP}$ 6.3 Hz), 64.28 d ($OCH_2$, $J_{CP}$ 5.9 Hz), 119.99 q ($CF_3$, $J_{CF}$ 317.7 Hz). $^{19}F$ NMR spectrum, $\delta_F$, ppm: –78.56. $^{31}P$ NMR spectrum, $\delta_P$, ppm: –1.18. In the $^1H$ and $^{13}C$ NMR spectra the signals of salt $(MeO)_2$·$(EtO)_2P^+$ $TfO^-$ are shifted downfield by ~0.1 ppm. The signals of salt $(EtO)_4P^+$ $TfO^-$ are overlapped with the signals of the other two salts. The $^{31}P$ signals in all salts practically coincide.

**Tris(dimethylamino)(hydroxy)phosphonium trifluoromethanesulfonate (XXIII)**. Yield 100%, transparent hygroscopic crystals. IR spectrum, ν, $cm^{-1}$: 2952, 2922, 1465, 1310, 1227, 1181, 1005, 764, 638, 515, 467. $^1H$ NMR spectrum, δ, ppm: 2.75 d (18H, $CH_3$, $J_{PH}$ 10.1 Hz), 11.13 s (1H, OH). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 36.37 d ($CH_3$, $J_{CP}$ 5.2 Hz), 119.94 q ($CF_3$, $J_{CF}$ 318.9 Hz). $^{19}F$ NMR spectrum, $\delta_F$, ppm: –78.55. $^{31}P$ NMR spectrum, $\delta_P$, ppm: 34.85. Found, %: P 9.89; S 10.49. $C_7H_{19}F_3N_3O_4PS$. Calculated, %: P 9.41; S 9.74.

**Tris(dimethylamino)(hydroxy)phosphonium bis(trifluoromethanesulfonyl)imide (XXIV)**. Yield 100%, a syrup-like mass or crystals. IR spectrum, ν, $cm^{-1}$: 3486, 2943, 2921, 1469, 1353, 1191, 1140, 1060, 1005, 764, 617, 571, 514. $^1H$ NMR spectrum, δ, ppm: 2.74 d (18H, $CH_3$, $J_{PH}$ 9.9 Hz), 9.05 s (1H, OH). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 36.51 d ($CH_3$, $J_{CP}$ 4.4 Hz), 119.65 q ($CF_3$, $J_{CF}$ 320.6 Hz). $^{19}F$ NMR spectrum, $\delta_F$, ppm: –78.82. $^{31}P$ NMR spectrum, $\delta_P$, ppm: 34.86. Found, %: C 20.60; H 4.09; F 24.74; N 12.12; P 5.73; S 13.93. $C_8H_{19}F_6N_4O_5PS_2$. Calculated, %: C 20.87; H 4.16; F 24.76; N 12.17; P 6.73; S 13.93.

**Tris(dimethylamino)(methoxy)phosphonium trifluoromethanesulfonate (XXV)**. Yield 87%, white crystals, mp 194°C. IR spectrum, ν, $cm^{-1}$: 3437, 2929, 1469, 1319, 1269, 1151, 1033, 1003, 761, 638, 518. $^1H$ NMR spectrum, δ, ppm: 2.85 d (18H, $NCH_3$, $J_{PH}$ 10.1 Hz), 3.99 d (3H, $OCH_3$, $J_{PH}$ 11.6 Hz). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 36.90 d ($NCH_3$, $J_{CP}$ 4.4 Hz), 56.09 d ($OCH_3$, $J_{CP}$ 6.6 Hz), 120.80 q ($CF_3$, $J_{CF}$ 320.7 Hz). $^{19}F$ NMR spectrum, $\delta_F$, ppm: –78.13. $^{31}P$ NMR spectrum, $\delta_P$, ppm: 38.76. Found, %: C 27.51; H 5.03; F 15.56; N 12.51; P 8.95; S 10.15. $C_8H_{21}F_3N_3O_4PS$. Calculated, %: C 27.99; H 6.17; F 16.60; N 12.24; P 9.02; S 9.34.

**Dimethoxy(hydroxy)phosphonium trifluoromethanesulfonate (XXVI)**. Yield 100%, light liquid. IR spectrum, ν, $cm^{-1}$: 2963, 2918, 2859, 2459, 1709, 1460, 1248, 1174, 1030, 639, 518. $^1H$ NMR spectrum, δ, ppm: 3.85 d (6H, $CH_3$, $J_{PH}$ 12.2 Hz), 6.91 d (1H, $J_{PH}$ 743.9 Hz), 15.08 s (1H, OH). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 53.81 d ($CH_3$, $J_{CP}$ 5.9 Hz), 119.48 q ($CF_3$, $J_{CF}$ 318.0 Hz). $^{19}F$ NMR spectrum, $\delta_F$, ppm: –78.43. $^{31}P$ NMR spectrum, $\delta_P$, ppm: 12.69 d.q ($J_{PH}$ 743.3, $J_{PCH}$ 11.8 Hz).

**Dimethoxy(hydroxy)phosphonium bis(trifluoromethanesulfonyl)imide (XXVII)**. Yield 100%, light brown liquid. IR spectrum, ν, $cm^{-1}$: 2966, 2919, 2861, 2468, 1695, 1351, 1331, 1196, 1143, 1057, 609, 574, 514. $^1H$ NMR spectrum, δ, ppm: 3.85 d (6H, $CH_3$, $J_{PH}$ 12.1 Hz), 6.80 d (1H, $J_{PH}$ 731.9 Hz), 11.77 s (1H, OH). $^{13}C$ NMR spectrum, $\delta_C$, ppm: 53.33 d ($CH_3$, $J_{CP}$ 5.5 Hz), 119.06 q ($CF_3$, $J_{CF}$ 321.3Hz). $^{19}F$ NMR spectrum, $\delta_F$, ppm: –77.29. $^{31}P$ NMR spectrum, $\delta_P$, ppm: 10.23 d.m ($^1J_{PH}$ 732.0).

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