ISSN 1070-4280, Russian Journal of Organic Chemistry, 2006, Vol. 42, No. 7, pp. 1097–1100. © Pleiades Publishing, Inc., 2006.
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SHORT COMMUNICATIONS

Dedicated to the Memory of Full Member
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Synthesis of 2-Ammonio(phosphonio)methyl-9-oxo-10-(4-heptyloxyphenyl)thioxanthenium Bis[hexafluorophosphates(V)]

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Received January 9, 2006

DOI: 10.1134/S1070428006070347

Onium salts, e.g., iodonium, sulfonium, and ammonium, are used as initiators of photopolymerization of unsaturated compounds [1–4]. Apart from salts containing a single cationic center, those possessing several cationic centers were reported; examples are disulfonium salts based on thioxanthen-9-one derivatives [5].

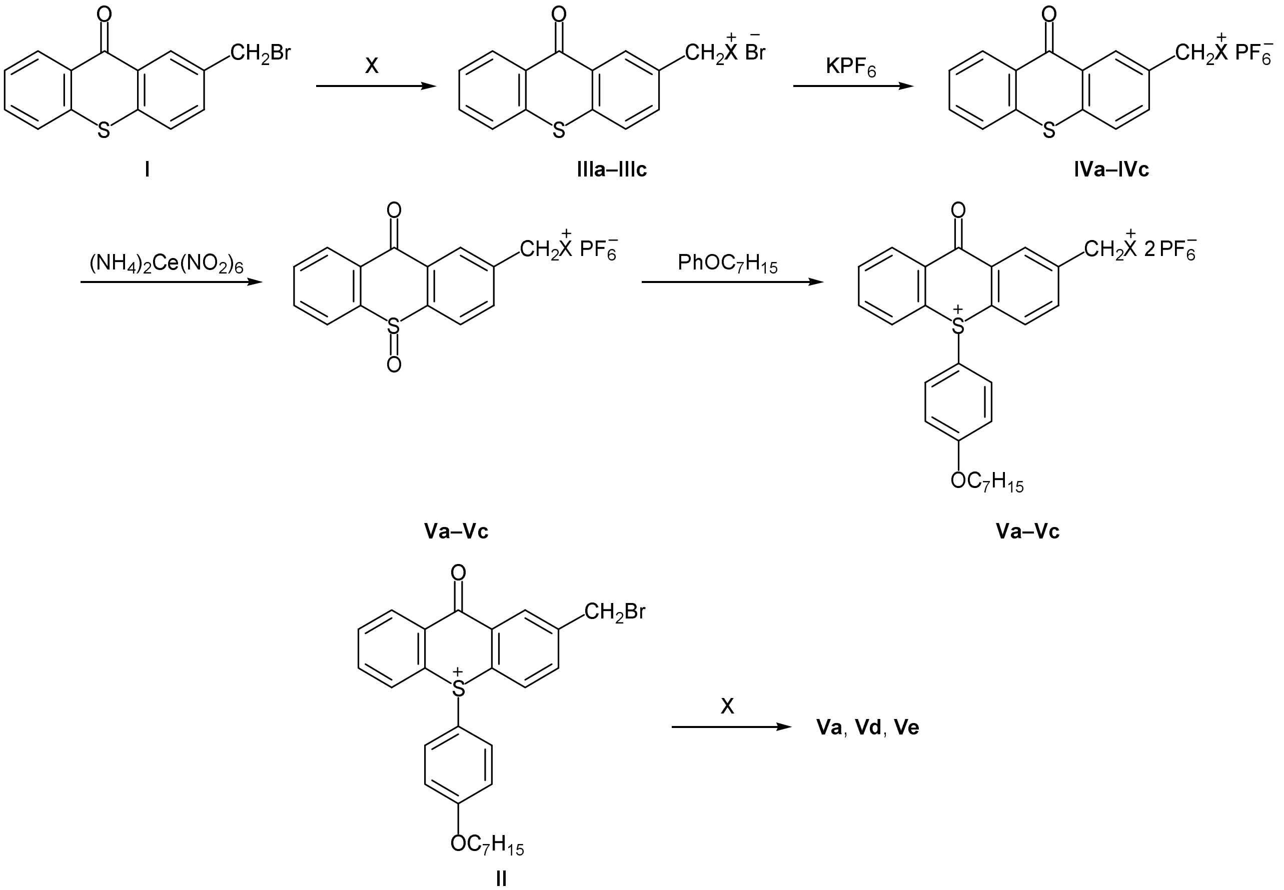
We previously [6] synthesized 10-(4-heptyloxyphenyl)-9-oxothioxanthenium hexafluorophosphates(V) by condensation of thioxanthene *S*-oxides with heptyloxybenzene. In the present communication we report on the synthesis of thioxanthenium bis[hexafluorophosphates(V)] which differ from known salts [5] by the presence of an additional ammonium or phosphonium substituent. We believe that compounds possessing several photochemically active centers with different initiating mechanisms may be used as efficient universal potoinitiators. The target compounds were synthesized in two ways starting from 2-bromomethylthioxanthen-9-one (**I**) and 2-bromomethyl-10-(4-heptyloxyphenyl)-9-oxothioxanthenium hexafluorophosphate(V) (**II**). According to the first of these, bromo derivative **I** was treated with bases (triethylamine, pyridine, or triphenylphosphine) to obtain the corresponding triethylammonium, pyridinium, and triphenylphosphonium bromides **IIIa**–**IIIc** which were converted into hexafluorophosphates(V) **IVa**–**IVc** via exchange reaction with KPF_6. Oxidation of salts **IVa**–**IVc** with cerium ammonium nitrate in acetonitrile gave sulfoxides **Va**–**Vc**, and condensation of the latter with heptyloxybenzene in methanesulfonic acid–phosphoric anhydride afforded thioxanthenium bis[hexafluorophosphates(V)] **VIa**–**VIc**.

The second route to salts **VI** included treatment of hexafluorophosphate(V) **II** with tertiary amines. The reaction of **II** with triethylamine gave bis[hexafluorophosphate(V)] **VIa** which was identical to a sample prepared from sulfoxide **Va** and heptyloxybenzene. Analogous reactions of salt **II** with *N,N*-dimethylbenzylamine and urotropin led to the formation of bis[hexafluorophosphates(V)] **VId** and **VIe**.

The structure of the products was confirmed by analytical and spectral methods. Initial compounds **I** and **II** were synthesized as described in [6].

Triethyl(9-oxo-9*H*-thioxanthen-2-ylmethyl)ammonium bromide (IIIa). A mixture of 1 mmol of compound **I**, 2 mmol of triethylamine, and 30 ml of chloroform was kept for 48 h at 20–25°C. The mixture was evaporated by half, and the precipitate was filtered off. Yield 75%, mp 225-228°C. IR spectrum: ν(C=O) 1640 cm^{-1}. ^1H NMR spectrum, δ, ppm: 1.34 t and 3.22 q (15H, Et, $J = 7.0$ Hz), 4.71 s (2H, CH_2), 7.63 t.d and 7.82 t.d (1H each, 6-H, 7-H, $J = 7.5$, 1.2 Hz), 7.88 m (2H, 3-H, 5-H), 8.01 d (1H, 4-H, $J = 8.20$ Hz), 8.48 d (1H, 8-H, $J = 7.80$ Hz), 8.60 d (1H, 1-H, $J = 1.40$ Hz). Found, %: C 58.54; H 6.29; Br 20.20; N 3.57; S 7.95. $C_{20}H_{24}BrNOS$. Calculated, %: C 59.11; H 5.91; Br 19.70; N 3.45; S 7.88.

1-(9-Oxo-9*H*-thioxanthen-2-ylmethyl)pyridinium bromide (IIIb) was synthesized in a similar way. Yield 84%, mp 245–247°C [7]. The IR spectrum of the product was identical to that given in [7]. ^1H NMR spectrum, δ, ppm: 6.07 s (2H, CH_2), 7.61 t.d and 7.79 t.d (1H each, 6-H, 7-H, $J = 8.0$, 1.5 Hz), 7.86 d.d (1H, 5-H, $J = 8.0$, 1.5 Hz), 7.95 m (2H, 3-H, 4-H), 8.21 t (2H, 3'-H, 5'-H, $J = 7.0$ Hz), 8.45 d.d (1H, 8-H,



X = NEt_3 (**a**), C_5H_5N (**b**), PPh_3 (**c**), $Me_2(PhCH_2)N$ (**d**), $C_6H_{12}N_4$ (**e**).

J = 8.0, 1.5 Hz), 8.65 m (2H, 1-H, 4'-H), 9.32 d (2H, 2'-H, 6'-H, *J* = 7.0 Hz). Found, %: Br 20.90; N 3.49; S 8.20. $C_{19}H_{14}BrNOS$. Calculated, %: Br 20.83; N 3.64; S 8.33.

(9-Oxo-9*H*-thioxanthen-2-ylmethyl)triphenylphosphonium bromide (IIIc). A mixture of 2 mmol of compound **I**, 2.3 mmol of triphenylphosphine, and 20 ml of toluene was heated for 1 h under reflux. The mixture was cooled, and the precipitate was filtered off. Yield 76%, mp 299–303°C. IR spectrum: ν(C=O) 1633 cm^{-1}. ^1H NMR spectrum, δ, ppm: 5.42 d (2H, CH_2, *J* = 15.6 Hz), 7.36 m (1H, 3-H), 7.58 t.d (1H, 6-H, *J* = 8.0, 1.0 Hz), 7.69–7.80 m (14H, 4-H, 7-H, *o*-H, *m*-H), 7.83 d (1H, 5-H, *J* = 8.0 Hz), 7.92 t.d (3H, *p*-H, *J* = 7.0, 2.0 Hz), 8.12 m (1H, 1-H), 8.39 d.d (1H, 8-H, *J* = 8.0, 1.0 Hz). Found, %: C 68.08; H 4.65; Br 14.10; S 5.80. $C_{32}H_{24}BrOPS$. Calculated, %: C 67.72; H 4.23; Br 14.11; S 5.64.

Triethyl(9-oxo-9*H*-thioxanthen-2-ylmethyl)ammonium, 1-(9-oxo-9*H*-thioxanthen-2-ylmethyl)pyridinium, and (9-oxo-9*H*-thioxanthen-2-ylmethyl)triphenylphosphonium hexafluorophosphates(V) IVa–IVc were obtained by adding a solution of 1.5–2 mmol of KPF_6 in 3–5 ml of water to a solution of 1 mmol of the corresponding bromide **IIIa–IIIc** in 15 ml of dimethyl sulfoxide.

Compound **IVa**. Yield 70%, mp 241–242°C. IR spectrum, ν, cm^{-1}: 1638 (C=O), 839 (P–F). ^1H NMR spectrum, δ, ppm: 1.35 t and 3.23 q (15H, 3Et, *J* = 7.0 Hz), 4.68 s (2H, CH_2), 7.63 t.d and 7.82 t.d (1H each, 6-H, 7-H, *J* = 8.0, 1.2 Hz), 7.84–7.90 m (2H, 3-H, 5-H), 7.99 d (1H, 4-H, *J* = 8.4 Hz), 8.47 d (1H, 8-H, *J* = 8.0 Hz), 8.61 d (1H, 1-H, *J* = 1.6 Hz). ^{19}F NMR spectrum: δ_F: 92.5 ppm, d (J_{FP} = 711.5 Hz). Found, %: C 50.64; H 5.19; F 24.22; N 3.08; S 6.76. $C_{20}H_{24}F_6NOPS$. Calculated, %: C 50.95; H 5.09; F 24.20; N 2.97; S 6.79.

Compound **IVb**. Yield 78%, mp 238–239°C. IR spectrum, ν, cm^{-1}: 1627 (C=O), 835 (P–F). ^1H NMR spectrum, δ, ppm: 6.03 s (2H, CH_2), 7.62 t.d and 7.81 t.d (1H each, 6-H, 7-H, *J* = 8.0, 1.5 Hz), 7.88 d.d (1H, 5-H, *J* = 8.0, 1.5 Hz), 7.95 m (2H, 3-H, 4-H), 8.20 m (2H, 3'-H, 5'-H), 8.46 d.d (1H, 8-H, *J* = 8.0, 1.5 Hz), 8.59–8.70 m (2H, 1-H, 4'-H), 9.27 m (2H, 2'-H, 6'-H). ^{19}F NMR spectrum: δ_F 92.4 ppm, d (J_{FP} = 711.1 Hz). Found, %: C 50.06; H 3.12; F 25.17; N 3.61; S 7.26. $C_{19}H_{14}F_6NOPS$. Calculated, %: C 50.78; H 3.12; F 25.39; N 3.12; S 7.13.

Compound **IVc**. Yield 87%, mp 222–224°C (from ethanol). IR spectrum, ν, cm^{-1}: 1635 (C=O), 841 (P–F). ^{1}H NMR spectrum, δ, ppm: 5.35 d (2H, CH_2, *J* = 15.8 Hz), 7.33 m (1H, 3-H), 7.58 t.d (1H, 6-H, *J* = 8.0, 1.5 Hz), 7.64–7.98 m (18H, 4-H, 5-H, 7-H, C_6H_5), 8.14 m (1H, 1-H), 8.40 d.d (1H, 8-H, *J* = 8.0, 1.5 Hz). Found, %: C 60.08; H 3.68; F 18.02; P 9.72; S 5.16. $C_{32}H_{24}F_6OP_2S$. Calculated, %: C 60.76; H 3.80; F 18.04; P 9.81; S 5.06.

Triethyl(9,10-dioxo-9*H*-10λ^4-thioxanthen-2-ylmethyl)ammonium, 1-(9,10-dioxo-9*H*-10λ^4-thioxanthen-2-ylmethyl)pyridinium, and (9,10-dioxo-9*H*-10λ^4-thioxanthen-2-ylmethyl)triphenylphosphonium hexafluorophosphates(V) Va–Vc were obtained by oxidation of 1 mmol of the corresponding hexafluorophosphate(V) **IVa–IVc** with 4 mmol of $(NH_4)_2Ce(NO_2)_6$ in 21 ml of a 3:1 acetonitrile–water mixture on stirring at 20–25°C for 2 h, followed by addition of 20 ml of water and cooling to 5°C.

Compound **Va**. Yield 85%, mp 199–205°C. IR spectrum, ν, cm^{-1}: 1675 (C=O), 1036 (S=O), 936 (P–F). ^{1}H NMR spectrum, δ, ppm: 1.34 t and 3.25 q (15H, 3Et), 4.73 s (2H, CH_2), 7.88 t.d and 8.02 t.d (1H each, 6-H, 7-H, *J* = 8.0, 1.5 Hz), 8.09 d.d and 8.17 d.d (1H each, 3-H, 5-H, *J* = 8.0, 1.5 Hz), 8.27 d (1H, 4-H, *J* = 8.0 Hz), 8.32 m (1H, 8-H), 8.42 d (1H, 1-H, *J* = 1.5 Hz). ^{19}F NMR spectrum: δ_F 92.4 ppm, d (J_{FP} = 711.1 Hz). Found, %: F 23.41; N 3.07; S 6.66. $C_{20}H_{24}F_6NO_2PS$. Calculated, %: F 23.41; N 2.87; S 6.57.

Compound **Vb**. Yield 92%, mp 230–233°C. IR spectrum, ν, cm^{-1}: 1663 (C=O), 1041 (S=O), 839 (P–F). ^{1}H NMR spectrum, δ, ppm: 6.09 s (2H, CH_2), 7.85 t.d and 7.99 t.d (1H each, 6-H, 7-H, *J* = 7.60, 1.12 Hz), 8.07–8.32 m (6H, 3-H, 4-H, 5-H, 8-H, 3'-H, 5'-H), 8.46 d (1H, 1-H, *J* = 1.12 Hz), 8.66 t (1H, 4'-H, *J* = 7.8 Hz), 9.26 d (2H, 2'-H, 6'-H, *J* = 6.8 Hz). ^{19}F NMR spectrum: δ_F 92.4 ppm (J_{FP} = 711.1 Hz). Found, %: N 3.39; S 6.86. $C_{19}H_{14}F_6NO_2PS$. Calculated, %: N 3.01; S 6.57.

Compound **Vc**. Yield 66%, mp 290–292°C. IR spectrum, ν, cm^{-1}: 1672 (C=O), 1033 (S=O), 838 (P–F). ^{1}H NMR spectrum, δ, ppm: 5.41 d (2H, CH_2, *J* = 16.0 Hz), 7.59 m (1H, 3-H), 7.68–7.80 m and 7.90–7.95 m (15H, $3C_6H_5$), 7.81–7.88 m (2H, 1-H, 7-H), 7.98 t.d (1H, 6-H, *J* = 7.0, 1.2 Hz), 8.04 d (1H, 4-H, *J* = 7.5 Hz), 8.13 d and 8.23 d (1H each, 5-H, 8-H, *J* = 7.0 Hz). Found, %: C 59.71; H 4.21; F 18.07; S 4.83. $C_{32}H_{24}F_6O_2P_2S$. Calculated, %: C 59.26; H 3.70; F 17.59; S 4.94.

2-(Triethylammoniomethyl)-, 2-(pyridiniomethyl)-, and 2-(triphenylphosphoniomethyl)-10-(4-heptyloxyphenyl)-9-oxo-9*H*-thioxanthen-10-ium bis[hexafluorophosphates(V)] VIa–VIc. A mixture of 4 ml of methanesulfonic acid–P_2O_5 (10:1), 0.18 g (0.9 mmol) of heptyloxybenzene, and 0.35 g (0.7 mmol) of hexafluorophosphate **Va–Vc** was stirred for 2.5 h at 20–25°C. Ice was then added to cool the mixture to 5°C, and a solution of 0.5 g (2.7 mmol) of KPF_6 in 5 ml of water was added. The mixture was stirred for 0.5 h, and the precipitate was filtered off, dried, and reprecipitated twice from methylene chloride with diethyl ether.

Compound **VIa**. Yield 0.35 g (60%), mp 126–128°C. IR spectrum, ν, cm^{-1}: 1677 (C=O), 841 (P–F). ^{1}H NMR spectrum, δ, ppm: 0.85 t (3H, CH_3, *J* = 6.6 Hz); 1.30 m, 1.69 m, and 3.24 q (25H, $5CH_2$, 3Et, *J* = 6.4 Hz); 4.07 t (2H, OCH_2, *J* = 6.4 Hz); 4.75 m (2H, CH_2N); 7.20 d and 7.96 d (4H, C_6H_4, *J* = 9.0 Hz); 8.00–8.20 m (5H, 3-H, 4-H, 5-H, 6-H, 7-H); 8.56 m (1H, 8-H); 8.67 m (1H, 1-H). ^{19}F NMR spectrum: δ_F 92.4 ppm, d (J_{FP} = 711.3 Hz). Found, %: C 48.82; H 5.32; F 27.91; N 2.00; S 3.98. $C_{33}H_{43}NO_2S \cdot 2PF_6$. Calculated, %: C 49.07; H 5.33; F 28.25; N 1.73; S 3.96.

Compound **VIb**. Yield 88%, mp 106–110°C. IR spectrum, ν, cm^{-1}: 1677 (C=O), 1636 ($C_5H_5N^+$), 840 (P–F). ^{1}H NMR spectrum, δ, ppm: 0.84 m (3H, CH_3), 1.25 m and 1.69 m (10H, $5CH_2$), 4.04 t (2H, OCH_2, *J* = 6.0 Hz), 6.10 s (2H, CH_2N), 7.17 d and 7.93 d (4H, C_6H_4, *J* = 9.0 Hz), 8.01 m (2H, 3'-H, 5'-H), 8.11 m (2H, 3-H, 4-H), 8.24 t (2H, 6-H, 7-H, *J* = 7.0 Hz), 8.55 m (2H, 5-H, 8-H), 8.62–8.72 m (2H, 1-H, 4'-H), 9.31 d (2H, 2'-H, 6'-H, *J* = 5.8 Hz). ^{19}F NMR spectrum: δ_F 92.5 ppm, d (J_{FP} = 711.3 Hz). Found, %: C 48.94; H 4.17; F 28.49; N 2.00; S 3.76. $C_{32}H_{33}NO_2S \cdot 2PF_6$ Calculated, %: C 48.92; H 4.20; F 29.04; N 1.78; S 4.07.

Compound **VIc**. Yield 92%, mp 115–120°C. IR spectrum, ν, cm^{-1}: 2930, 2850 (C–H); 1676 (C=O), 840 (P–F). ^{1}H NMR spectrum, δ, ppm: 0.86 m (3H, CN_3), 1.09 m and 1.71 m (10H, $5CH_2$), 4.09 t (2H, OCH_2, *J* 6.0 Hz), 5.45 m (2H, CH_2P), 7.26 d and 7.47 d (4H, C_6H_4, *J* = 8.8 Hz), 7.52–8.03 m (20H, 3-H, 4-H, 5-H, 6-H, 7-H, $3C_6H_5$), 8.19 m (1H, 1-H), 8.48 m (1H, 8-H). ^{19}F NMR spectrum: δ_F 92.48 ppm, d (J_{FP} = 711.7 Hz). Found, %: C 55.38; H 4.39; S 3.86.

$C_{45}H_{43}O_2PS \cdot 2PF_6$. Calculated, %: C 55.78; H 4.44; S 3.30.

Reaction of salt II with amines. A solution of 0.5 mmol of compound **II** and 0.7–1 mmol of triethylamine, *N*,*N*-dimethylbenzylamine, or urotropin in 20 ml of chloroform was kept for 30 h at 20–25°C. In the reaction with triethylamine, the mixture was cooled to 0°C, and the precipitate was filtered off and washed with diethyl ether. Yield of salt **VIa** 0.13 g (32%), mp 123–126°C (from ethanol). The IR and ^{1}H and ^{19}F NMR spectra of the product were identical to those of a sample prepared as described above from sulfoxide **Va** and heptyloxybenzene.

In the reactions with *N*,*N*-dimethylbenzylamine and urotropin, the mixture was evaporated almost to dryness, the residue was dissolved in 10 ml of DMSO, a solution of 1 mmol of KPF_6 in 3 ml of water was added, and compound **VId** or **VIe** was filtered off, dried, and reprecipitated from ethanol with diethyl ether.

2-(*N*-Benzyl-*N*,*N*-dimethylammoniomethyl)-10-(4-heptyloxyphenyl)-9-oxo-9*H*-thioxanthenium bis[hexafluorophosphate(V)] (VId). Yield 55%, mp 140–145°C (from ethanol). IR spectrum, ν, cm^{-1}: 1676 (C=O), 840 (P–F). ^{1}H NMR spectrum, δ, ppm: 0.85 m (3H, $\mathbf{CH}_3CH_2$), 1.25 m and 1.71 m (10H, $5CH_2$), 2.92 s and 2.95 s (3H each, CH_3), 4.06 t (2H, OCH_2, J = 6.2 Hz), 4.65 s and 4.82 s (4H, $2CH_2N$), 7.20 d and 7.96 d (4H, C_6H_4, J = 9.2 Hz), 7.61 br.s (5H, C_6H_5), 8.02 m (3H, 5-H, 6-H, 7-H), 8.18 m (2H, 3-H, 4-H), 8.56 m (1H, 8-H), 8.77 m (1H, 1-H). Found, %: C 51.52; H 4.54; F 26.97; N 2.01; S 4.23. $C_{36}H_{41}NO_2S \cdot 2PF_6$. Calculated, %: C 51.37; H 4.87; F 27.11; N 1.66; S 3.80.

2-(1,3,5,7-Tetraazatricyclo[3.3.1.1^{3,7}]decan-1-iomethyl)-10-(4-heptyloxyphenyl)-9-oxo-9*H*-thioxanthenium bis[hexafluorophosphate(V)] (VIe). Yield 42%, mp 173–178°C. IR spectrum, ν, cm^{-1}: 2932, 2858 (C–H); 1679 (C=O); 843 (P–F). ^{1}H NMR spectrum, δ, ppm: 0.85 m (3H, CH_3), 1.28 m and 1.52 m (10H, $5CH_2$), 4.07 t (2H, OCH_2, J = 6.5 Hz), 4.27–4.68 m (8H, $4CH_2N^+$), 5.10 br.s (6H, $3CH_2N$), 7.20 d and 7.95 d (4H, C_6H_4, J = 8.8 Hz), 7.99–8.24 m (5H, 3-H, 4-H, 5-H, 6-H, 7-H), 8.58 m (1H, 8-H), 8.67 m (1H, 1-H). ^{19}F NMR spectrum: δ_F 92.49 ppm, d (J_{FP} = 711.3 Hz). Found, %: C 47.01; H 4.68; N 6.63; S 4.20. $C_{33}H_{40}N_4O_2S \cdot 2PF_6$. Calculated, %: C 46.81; H 4.73; N 6.62; S 3.78.

The IR spectra were recorded in KBr on a Vector-22 instrument. The ^{1}H and ^{19}F NMR spectra were measured on a Bruker AC-200 spectrometer from solutions in DMSO-d_6 using the residual solvent signal as reference for ^{1}H; the ^{19}F chemical shifts were determined relative to C_6F_6 as reference. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using benzene or chloroform as eluent.

This study was performed under financial support by the Presidium of the Russian Academy of Sciences (project no. 8-3) and by the Siberian Division of the Russian Academy of Sciences (integration project nos. 15, 17, and 33).

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