Synthesis of a Novel Perfluorinated Vinyl Ether Containing Sulfonimide and Phosphonic Acid Functionalities†

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The novel perfluorinated vinyl ether containing sulfonimide and phosphonic acid functionalities, $CF_2=CFOCF_2CF(CF_3)OCF_2CF_2SO_2NHSO_2(CF_2)_2P(O)(OH)_2$, has been synthesized by multiple reaction steps. It is a very strong bi-functional acid and exhibits a high degree of stability in aqueous solution at an elevated temperature. These properties make it an attractive monomer for the preparation of the co-polymer with TFE to obtain the high quality ionomer membrane and proton conductor.

Keywords perfluorinated vinyl ether, sulfonimide, phosphonic acid

Introduction

In the past decades, considerable research work has been focused on the fluorinated ionomers[1-4] which have exceptional thermal and chemical stabilities.[5] Therefore they have shown special applications, such as membrane separation in the electrochemical processes and superacid catalysts in organic synthesis.[6,7] Recently we have developed a new type of perfluorinated ionomers containing the bis(perfluoroalkylsulfonyl)imide functionality in the side chain.[8] The remarkable acidity of the fluorinated sulfonimide $(R_fSO_2)_2NH$ is expected to impart unusual properties to this superacid polymer. In addition, a variety of fluorinated phosphonic acid and a mixed perfluoralkylsulfonic acid/phosphonic acid[9,10] have been synthesized for evaluation as potential fuel cell electrolytes. The fluorinated phosphonic acids exhibit much stronger acidity and thermal stability than their nonfluorinated analogues.[9] After successful preparation of the mixed perfluoroalkylsulfonimide/sulfonic acid $R_fSO_2NHSO_2(CF_2)_nSO_3H$,[11] our interest is now focused on the synthesis of the mixed perfluoroalkylsulfonimide/phosphonic acid.

This paper reports the synthesis of ethyl 3-oxa-5-(trifluoromethylsulfonimido sulfonyl)octafluoropentyl phosphonate, $CF_3SO_2NHSO_2(CF_2)_2O(CF_2)_2P(O)(OEt)_2$, and the novel fluorinated vinyl ether containing the superacidic sulfonimide and phosphonic acid groups, $CF_2=CFOCF_2CF(CF_3)OCF_2CF_2SO_2NHSO_2(CF_2)_2O(CF_2)_2P(O)(OH)_2$. Its co-polymer with tetrafluoroethylene (TFE) is expected to be a potential proton conductor and to have high ion selectivity for using in the chloro-alkali industry as an ionomer membrane.

Results and discussion

The starting material for the preparation of the mixed fluorinated sulfonimide and phosphonic acid is $CF_2=CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$ (**1**). The chloronation of the C=C bond in **1** afforded compound **2**, which was treated with liquid NH_3 at −78 ℃, followed by MeONa/MeOH resulting in the conversion of the sulfonylfluoride to sulfonimide sodium salt $R_fSO_2NH(Na)$ (**3**) (R_f:

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$ClCF_2CFClOCF_2CF(CF_3)OCF_2CF_2$). The silylated sulfonimide $R_fSO_2N(Na)SiMe_3$ (**4**) was obtained by heating **3** with excess of $(Me_3Si)_2NH$.[12] **4** smoothly reacted with $I(CF_2)_2O(CF_2)_2SO_2F$ to give $R_fSO_2N(Na)SO_2(CF_2)_2O(CF_2)_2I$ (**5**) in good yield (Scheme 1). The conversion of R_fI into $R_fP(O)(OEt)_2$ was achieved by heating of R_fI with tetraethyl pyrophosphite $(EtO)_2POP(OEt)_2$ in autoclave[9,10] or irradiation by UV[13] to obtain $R_fP(OEt)_2$ which was then oxidized with peroxide such as $^tBuOOBu^t$ or ^tBuOOH giving $R_fP(O)(OEt)_2$. To avoid the use of the expensive $(EtO)_2POP(OEt)_2$, we tried to use the cheaper $ClP(O)(OEt)_2$ to react with corresponding fluoroalkyl magnesium halide R_fMgX, which could be prepared by treatment of R_fI with $RMgX/Et_2O$ at low temperature. First a model reaction was tried using the more easily available starting material $CF_3SO_2N(Na)SO_2(CF_2)_2O(CF_2)_2I$ (**11**) obtained from the reaction of $CF_3SO_2N(Na)SiMe_3$ (**10**)[13] with $I(CF_2)_2O(CF_2)_2SO_2F$. **11** was treated with CH_3MgCl/Et_2O at -50 ℃ followed by an equal mole amount of $ClP(O)(OEt)_2$. Workup of the reaction mixture with HCl (3 N) and vacuum distillation gave the expected product $CF_3SO_2NHSO_2(CF_2)_2O(CF_2)_2P(O)(OEt)_2$ (**12**) in 60% yield (Scheme 2). A byproduct $CF_3SO_2NHSO_2(CF_2)_2O(CF_2)_2H$ (18%) was found in the ^{19}F NMR spectrum which came from the hydrogen-abstraction of the intermediate $CF_3SO_2N(Na)SO_2(CF_2)_2O(CF_2)_2MgCl$.

A similar reaction of **5** with CH_3MgCl in absolute ether in a very dried vessel followed by the treatment with $ClP(O)(OEt)$ gave 65% yield of **6** (Scheme 1). The ^{19}F NMR spectra showed the large difference between products **6** and **5**. For compound **5** the chemical shift of ICF_2 is singlet at δ -67.4, for product **6**, a doublet at δ -123.9, -124.5 ($^2J_{P\text{-}F}$ = 84 Hz) corresponds to the PCF_2 absorption. Dechlorination of **6** by zinc powder gave the difunctional fluorinated vinyl ether **7**, which was then

Scheme 1

$CF_2=CFOCF_2CF(CF)_3OCF_2CF_2SO_2F$ —a→ **1**

$ClCF_2CFClOCF_2CF(CF_3)OCF_2CF_2SO_2F$ —b→ **2**

$R_fSO_2NH_2$ (**3**) —c→ $R_fSO_2N(Na)SiMe_3$ (**4**) —d→

$R_fSO_2N(Na)SO_2(CF_2)_2O(CF_2)_2I$ —e→ **5**

$R_fSO_2N(Na)SO_2(CF_2)_2O(CF_2)_2P(O)(OEt)_2$ —f→ **6**

$CF_2=CFOCF_2CF(CF_3)OCF_2CF_2SO_2N(Na)SO_2(CF_2)_2O(CF_2)_2P(O)(OEt)_2$ —g→ **7**

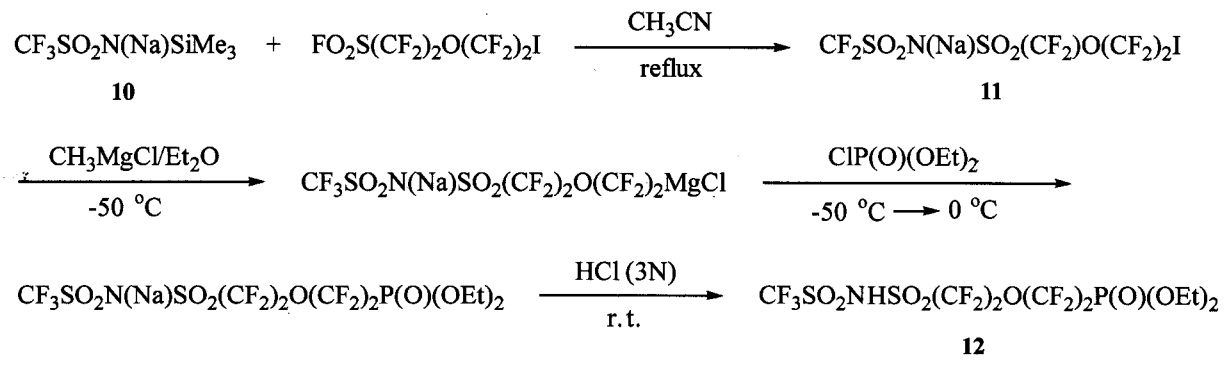
$CF_2=CFOCF_2CF(CF_3)OCF_2CF_2SO_2NHSO_2(CF_2)_2O(CF_2)_2P(O)(OH)_2$ —h→ **8**

$CF_2=CFOCF_2CF(CF_3)OCF_2CF_2SO_2N(Na)SO_2(CF_2)_2O(CF_2)_2P(O)(ONa)_2$ **9**

For **3**, **4**, **5** and **6** R_f=$ClCF_2CFClOCF_2CF(CF_3)OCF_2CF_2$

Reaction conditions and yields: (a) Cl_2, r.t., 8 h, 96%. (b) NH_3, -78 ℃. (c) 1. NaOMe/NaOH, 92%; 2. HMDS, 110 ℃, 36 h, 92%. (d) $I(CF_2)_2O(CF_2)_2SO_2F/CH_3CN$, reflux 48 h, 83%. (e) 1. CH_3MgBr/Et_2O, -50 ℃, 5 h; 2. $ClP(O)(OEt)_2$, -50 ℃, 1 h, r.t., 65%. (f) Zn/Ac_2O, 100 ℃, 8 h, 95%. (g) HCl (11 N), 100 ℃, 12 h, 62%. (h) Na_2CO_3, CH_3CN/H_2O, 100%.

Scheme 2



hydrolyzed with concentrated hydrochloric acid affording the mixed fluoroalkyl sulfonimide-phosphonic acid **8** (Scheme 1). To obtain the pure acid, a molecular distillation apparatus was used for the distillation of the crude product. **8** is a colourless, high boiling point and very hydroscopic liquid. It was also noticed that, after heating 8 h at 130—140 ℃, the carbon-carbon double bond in the acid remained unchanged. **8** can be dissolved in water, and titration of its aqueous solution with sodium hydroxide (0.001 N) gave rise to two inflection points, one for 2 equivalents (the NH and one phosphonic acid) and the other for 1 equivalent (the second phosphonic acid proton). The total titre for **8** gave 99.2% of a tribasic acid based on the molecular weight of 803 g/mol. Because **8** is a very hydroscopic liquid with very high boiling point, the easily handled sodium salts **7** or **9** are used to copolymerize with TFE, and this process and the chemical and physical properties of the co-polymers are under investigation.

In summary, a successful route to the novel perfluorinated vinyl ether containing the mixed sulfonimide and phosphonic acid functionalities has been developed from the readily available precursors. Further work will concentrate to the application and bulk scale synthesis of this novel monomer.

Experimental

Trifluoromethylsulfonyl fluoride was kindly provided by 3M Co., and 3-oxa-5-iodo-octafluoropentylsulfonyl fluoride was obtained from Shanghai Institute of Organic Chemistry. IR spectra were obtained using a Perking-Elmer 1430 ratio recording instrument or a Perking-Elmer 1600FT-IR instrument. ^{19}F NMR and ^{1}H NMR spectra were recorded on an IBM NR 200AF spectrometer using $CFCl_3$ and TMS as the internal standards, using CD_3CN or $CDCl_3$ as solvent. ^{19}F NMR chemical shift is positive when found at a lower field than that of $CFCl_3$. For the ^{31}P NMR, H_3PO_4(85%) was used as the external standard. MS spectra were obtained on an HP-Hewlett packed GC-MS 5890 instrument. The boiling points and melting points are uncorrected.

Preparation of compound **2**[14]

a b c d e f g h
$ClCF_2CFClOCF_2CF(CF_3)OCF_2CF_2SO_2F$

Into a one-necked 500-mL flask containing **1** (13.4 g, 30 mmol) and a magnetic stirring bar, chlorine gas (40 mmol) was introduced at −196 ℃. The mixture was warmed to room temperature and stirred for 12 h. After removing the excess Cl_2, the residue was distilled under reduced pressure giving **2** (14.7 g, 95%). B.p. 42 ℃/0.5 Pa; ^{19}F NMR ($CDCl_3$) δ: −71.3 (s, F_a), −76.9 (m, F_b), −78.8—−9.8 (m, F_c), −145.5 (t, Hz, F_d), −80.2 (s, F_e), −82.6—−85.6 (m, F_f), −112.6 (s, F_g), +45.3 (t, Hz, F_h); IR (KCl) ν: 1463 (s), 1296 (s), 1238 (s), 1182 (s), 1139 (s), 1112 (s), 1024 (s), 980 (s), 920 (s), 857 (m), 842 (m), 820 (s), 690 (m), 604 (s), 582 (m), 502 (m) cm^{-1}.

Preparation of compound **3**

a b c d e f g
$CF_2ClCFClOCF_2CF(CF_3)OCF_2CF_2SO_2NH_2$

2 (5.2 g, 10 mmol) was treated with excess liquid NH_3, then H_2SO_4(98%, 1.5 mL) was added, the reaction mixture was stirred for 4 h at 40 ℃ to remove HF. Vacuum distillation gave **3** (5 g, 95%). B.p. 80—82

℃/0.5 Pa; ^{19}F NMR ($CDCl_3$) δ: −70.7 (s, F_a), −76.5 (m, F_b), −77.6—−78.2 (m, F_c), −144.9 (t, F_d), −79.3 (s, F_e), −83.4—−84.1 (m, F_f), −116.7 (s, F_g); IR (KCl) ν: 3393 (s), 3307 (s), 1542 (m), 1392 (s), 1312 (s), 1240 (s), 1181 (s), 1139 (s), 1207 (s), 985 (s), 977 (m), 918 (m), 864 (m), 722 (m), 606 (m), 576 (m) cm^{-1}. Anal. calcd for $C_7H_2O_4NF_{13}Cl_2S$: C 16.36, H 0.39, N 2.72, F 48.05; found C 16.01, H 0.80, N 2.92, F 47.88.

Preparation of **4**

$$\overset{a}{Cl}\overset{b}{CF_2}\overset{c}{CFCl}\overset{d}{OCF_2}\overset{e}{CF}(CF_3)\overset{f}{OCF_2}\overset{g}{CF_2}SO_2N(Na)SiMe_3$$

3 (5 g, 9.7 mmol) was treated with MeONa (0.52 g, 9.7 mmol) in MeOH (10 mL). After removing the solvent, the residue was dried throughout under vacuum line for 12 h at 50 ℃. The sodium salt was refluxed with HMDS (30 mL) for 48 h giving **4** (5.3 g, 91%) which was a very hydroscopic white solid. ^{19}F NMR ($CDCl_3$) δ: −70.5 (s, F_a), −76.4 (m, F_b), −77.8—−78.2 (m, F_c), −144.7 (t, F_d), −78.9 (s, F_e), −82.0—−84.0 (m, F_f), −116.5 (s, F_g); ^{1}H NMR ($CDCl_3$) δ: 0.04 (s, 3H, CH_3).

Preparation of **5**

$$ClCF_2CFClOCF_2CF(CF_3)OCF_2CF_2SO_2N(Na)SO_2CF_2\text{-}CF_2OCF_2CF_2I$$

A mixture of **4** (5.3 g, 8.7 mmol), anhydrous CH_3CN (20 mL) and $I(CF_2)_2O(CF_2)_2SO_2F$ (6.4 g, 15 mmol) in a 50-mL flask was heated for 48 h at 85—90 ℃. After removing the solvent and excess sulfonyl fluoride, the residue was dried under vacuum to give the crude product **5** (6.5 g, 80%). Pure **5** was obtained by acidifying the crude product with HCl (3 mL, 11 N), extracting with Et_2O and vacuum distillation giving **5a**:

$$\overset{a}{CF_2}\overset{b}{ClCFCl}\overset{c}{OCF_2}\overset{d}{CF}\overset{e}{(CF_3)}\overset{f}{OCF_2}\overset{g}{CF_2}SO_2NH\overset{h}{SO_2}\overset{i}{CF_2}\overset{j}{CF_2}\text{-}\overset{k}{OCF_2CF_2I}$$

(b.p. 112—118 ℃/0.4 Pa) which was then neutralized back to the sodium salt by Na_2CO_3. ^{19}F NMR ($CDCl_3$) δ: −71.3 (s, F_a), −77.4 (m, F_b), −78.2—−78.6 (m, F_c), −145.8 (t, F_d), −80.2 (s, F_e), −84.8—−85.8 (m, F_f), −113.6 (s, F_g), −113.3 (s, F_h), −85.9 (m, F_i), −81.5 (m, F_j), −65.6 (s, F_k); ^{1}H NMR ($CDCl_3$, 300 Hz) δ: 9.94 (s, NH); IR (AgCl) ν: 3362 (m), 3259 (m), 1340 (m), 1320 (m), 1243 (s), 1182 (vs), 1136 (vs), 1204 (m), 975 (m), 906 (s), 719 (m), 510 (m) cm^{-1}; MS *m/z* (%): 840 (M^+H-SO_2-O, 0.1), 508 ($M^+H-ClCF_2CFClOCF_2CF(CF_3)OSO_2NH$, 1.7), 408 ($M^+H-ClCF_2CFClOCF_2CF(CF_3)OCF_2CF_2SO_2NH$, 1.1), 227 ($ICF_2CF_2^+$, 20.2), 185 ($ClC_3F_6^+$, 2.4), 177 ($ICF_2^+$, 16.2), 151 ($ClCF_2CFCl^+$, 56.8), 142 ($(SO_2)_2N^+$, 2.5), 127 ($I^+$, 64.7), 119 ($C_2F_3^+$, 45.9), 110 ($SO_2NS^+$, 16.9), 85 ($ClCF_2^+$, 44.4), 78 ($S_2N^+$, 5.6), 69 ($CF_3^+$, 96.9), 64 ($SO_2^+$, 100). Anal. calcd for $C_{11}HNO_7S_2F_{21}Cl_2I$: C 14.36, H 0.11, N 1.52, F 43.36; found C 14.92 H 0.12, N 1.41, F 42.97.

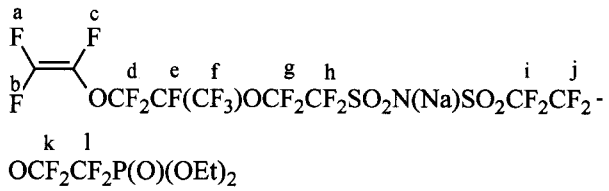
Preparation of **6**

$$\overset{a}{Cl}\overset{b}{CF_2}\overset{c}{CFCl}\overset{d}{OCF_2}\overset{e}{CF}(CF_3)\overset{f}{OCF_2}\overset{g}{CF_2}SO_2N(Na)\overset{h}{SO_2}CF_2\text{-}\overset{i}{CF_2}\overset{j}{OCF_2}\overset{k}{CF_2}P(O)(OEt)_2$$

CH_3MgCl/Et_2O (2 mL, 3 mol/L) was injected into a 50 mL flask containing a solution of **5** (4.7 g, 5 mmol) and anhydrous ether (20 mL) at −50 ℃. After stirring at this temperature for 0.5 h, $ClP(O)(EtO)_2$ (0.9 g, 5.1 mmol) was added, the reaction mixture was stirred for another 1 h and then warmed to 0 ℃. HCl (5 mL, 6 N) and ice water (5 mL) were added, the ether layer was separated, and the aqueous layer was extracted with Et_2O (2 × 10 mL). After evaporating the ether, residue was fractionally distillated giving $ClCF_2CFClOCF_2CF(CF_3)\text{-}OCF_2CF_2SO_2NHSO_2(CF_2)_2O(CF_2)_2P(O)(OEt)_2$, which was neutralized by Na_2CO_3 to afford the salt **6** (3.1 g, 65%) after dried under vacuum for 24 h at 80 ℃. ^{19}F NMR (CD_3CN) δ: −71.3 (s, F_a), −77.3 (m, F_b), −78.9—−79.3 (m, F_c), −145.9 (t, F_d), −80.2 (s, F_e), −83.7 (m, F_f), −111.7 (s, F_g), −117.3 (s, F_h), −82.2 (m, F_i), −83.8 (m, F_j), −125.5 (d, $^2J_{P-F}$ = 84 Hz, F_k); ^{1}H NMR ($CDCl_3$, 300 Hz) δ: 1.33 (m, 3H), 4.20 (m, 2H); ^{31}P NMR δ: −1.41 (t, $^2J_{F-P}$ = 84 Hz); IR (KCl) ν: 2994 (m), 2932 (w), 1445 (w), 1340 (s), 1312 (s), 1258 (s), 1226 (s), 1070 (s), 1016 (s), 982 (s), 968 (m), 863 (m), 797 (m), 686 (s), 649 (m), 502

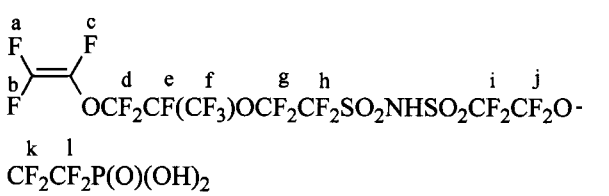
(m) cm^{-1}. Anal. calcd for $C_{15}H_{11}NO_{10}S_2F_{21}Cl_2P$: C 19.37, H 1.19, N 1.51, F 42.89; found C 19.05, H 1.21, N 1.49, F 42.47.

Preparation of **7**



A mixture of **6** (3.1 g, 3.3 mmol), zinc powder (1.5 g, 11 mmol) and Ac_2O (10 mL) in a 50 mL flask was heated at 100 ℃ for 9 h, the excess zinc powder and the *in-suit* formed $ZnCl_2$ were removed by filtration, and the filtrate was heated to 80 ℃ under vacuum for 4 h giving the crude product **7** (2.6 g, 91%) which was recrystallised from CH_3CN and EtOH (1:1) to give pure product. M. p. 210—215 ℃; ^{19}F NMR (CD_3CN) δ: −112.4 (d-d, F_a), −120.8 (d-d, F_b), −135.6 (d-d, F_c), −77.8 (m, F_d), −144.3 (t, F_e), −79.1 (s, F_f), −80.3 (m, F_g), −115.9 (s, F_h), −117.4 (s, F_i), −82.0 (m, F_j), −83.6 (m, F_k), −124.0 (d, F_l); ^{1}H NMR ($CDCl_3$, 300 Hz) δ: 1.30 (m, 3H), 4.16 (m, 2H); ^{31}P NMR δ: −3.25 (t, $^2J_{P-F}$ = 84 Hz); IR (KCl) ν: 2986 (s), 2934 (m), 1483 (w), 1561 (s), 1339 (s), 1279 (s), 1228 (s), 1163 (s), 1036 (s), 977 (s), 801 (m), 744 (m), 720 (m), 603 (m), 502 (m) cm^{-1}. Anal. calcd for $C_{15}H_{10}NO_{10}S_2F_{21}PNa$: C 20.44, H 1.14, N 1.59, F 45.27; found C 20.02, H 1.46, N 1.26, F 45.06.

Preparation of **8**

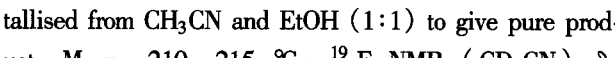


A mixture of **7** (2.06 g, 3 mmol) and HCl (11 N, 3 mL) was stirred for 12 h at 100 ℃. Ice water (5 mL) was added, and this mixture was extracted with Et_2O (2 × 10 mL). After evaporation, the residue was distilled using a molecular distiller at 130—140 ℃ under 0.4 Pa giving **8** (1.4 g, 62%). ^{19}F NMR (CD_3CN) δ: −112.3 (d-d, F_a), −120.7 (d-d, F_b), −135.7 (d-d, F_c), −77.4 (m, F_d), −144.0 (t, F_e), −79.2 (s, F_f), −82.4—−84.6 (s, F_g), −113.2 (s, F_h), −114.5 (s, F_i), −81.0 (m, F_j), −83.8 (m, F_k), −126.6 (d, F_l); ^{1}H NMR ($CDCl_3$, 300 Hz) δ: −11.8 (NH and OH). Anal. calcd for $C_{11}H_3NO_{10}S_2F_{21}P$: C 16.45, H 0.38, N 1.74, F 49.67; found C 16.08, H 0.71, N 1.40, F 49.32.

Titration of **8**

Titration of **8** (0.072 g) was monitored using an acument pH meter 925 with NaOH solution (0.001 N) at 22 ℃. The total titre for **8** gave 99.2% of a tribasic acid based on an anhydrous molecular weight of 803 g/mol.

Preparation of **12**



A mixture of $CF_3SO_2N(Na)SiMe_3$ (1.29 g, 5 mmol) was prepared according to the literature method,[12] CH_3CN (15 mL) and $I(CF_2)_2O(CF_2)_2SO_2F$ (4.3g, 10 mmol) was heated at 85—90 ℃ for 48 h. After removing the solvent and excess $I(CF_2)_2O(CF_2)_2SO_2F$, the residue was dried under vacuum at 60 ℃ for 24 h giving the hydroscopic solid $CF_3SO_2N(Na)SO_2(CF_2)_2O(CF_2)_2I$ (**11**) (2.6 g, 91%). ^{19}F NMR (CD_3CN) δ: −67.5 (s, ICF_2), −81.0 (m, CF_2O), −85.1 (m, OCF_2), −116.3 (s, SCF_2), −79.0 (s, CF_3). A solution of **11** (2.6 g, 4.5 mmol) in 10 mL of anhydrous ether was treated by CH_3MgCl/Et_2O (3 mol/L, 2 mL) at −50 ℃ for 5 h, followed by $ClP(O)(OEt)_2$ (0.9 g, 5 mmol) and similar working up as preparation of compound **6** gave **12** (1.6 g, 61%). ^{19}F NMR (CD_3CN) δ: −79.2 (s, F_a), −116.0 (s, F_b), −80.5 (m, F_c), −83.1 (m, F_d), −124.9 (d, $^2J_{F-P}$ = 84 Hz, Fe); ^{1}H NMR ($CDCl_3$, 300 Hz) δ: 10.9 (s, 1H), 4.30 (m, 2H), 1.38 (m, 3H); ^{31}P NMR δ: −3.10 (t); IR (AgCl) ν: 3450 (s), 3231 (m), 2997 (m), 2885 (w), 1462 (m), 1346 (s), 1330 (s), 1200 (s), 1175 (s), 1145 (s), 1043 (s), 977 (m), 608 (m), 581 (m) cm^{-1}; MS *m/z* (%): 566 (M^+H, 82), 565 (M^+, 88), 564 (M − H, 96), 565 ($M^+ - C_2H_5$, 100).

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