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Synthesis, Structure, and Reactions of Triphenylphosphine *N*-((Perfluoroalkyl)sulfonyl)imine and Triphenylarsine *N*-((Perfluoroalkyl)sulfonyl)imine

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Introduction

Phosphine imine compounds were first prepared via the reaction of tertiary phosphines with organic azide 70 years ago.[1] To date, various types of iminophosphoranes have been prepared. For example, triphenylphosphine *N*-tosylimine[2] was synthesized from *N*-sulfinyl-*p*-toluenesulfonamide, TsNSO, and triphenylphosphine sulfide, $\mathrm{Ph_3P{=}S}$, or triphenylphosphine phenylimine, and the triphenylarsine *N*-tosylimine[3] could also be prepared from Chloramine-T and triphenylarsine (eqs 1 and 2).

$$\mathrm{TsNSO + Ph_3PS \rightarrow TsN{=}PPh_3 + S_2O} \qquad (1)$$

$$\mathrm{RSO_2NClNa + PR'_3 \rightarrow RSO_2N{=}PR'_3 + NaCl} \qquad (2)$$

The synthesis of fluorine-containing analogues has attracted much more attention in recent years. The presence of a fluorine atom leads to profound changes of physical and biological properties of the molecules (pK_a, lipoidal solubility, etc.).

The syntheses of *N*-(perfluoroalkyl)sulfonyl-substituted stibine imine, $\mathrm{R_fSO_2N{=}SbPh_3}$,[4] and bismuthine imine, $\mathrm{R_fSO_2N{=}BiPh_3}$,[5] were reported, and it was found that as $\mathrm{CF_3SO_2N{=}}$ is a strong electron-withdrawing group,[6,7] the introduction of $\mathrm{R_fSO_2N{=}}$ into molecules can change their chemical properties prominently (eqs 3 and 4).

$$\mathrm{CF_3SO_2N_3 + SbPh_3 \rightarrow CF_3SO_2N{=}SbPh_3 + N_2} \qquad (3)$$

$$\mathrm{CF_3SO_2N(SiMe_3)_2 + Ph_3BiF_2 \rightarrow CF_3SO_2N{=}BiPh_3 + 2Me_3SiF} \qquad (4)$$

Results and Discussion

In the present paper, we described a new method for the preparation of *N*-(perfluoroalkyl)sulfonyl-substituted phosphine imine and arsine imine, $\mathrm{R_fSO_2N{=}EPh_3}$ (E: P, As). These two imines were obtained from the reactions of *N*,*N*-dichloroperfluoroalkanesulfonamides $\mathrm{R_fSO_2NCl_2}$[8] with triphenylphosphine or triphenylarsine in the presence of zinc powder (eq 5).

$$\underset{\mathbf{1}}{\mathrm{EPh_3}} + \underset{\mathbf{2}}{\mathrm{R_fSO_2NCl_2}} \xrightarrow[\mathrm{C_6H_6\ or\ Et_2O}]{\mathrm{Zn}} \underset{\mathbf{3}\ (72-78\%)}{\mathrm{R_fSO_2N{=}EPh_3}} \qquad (5)$$

$\mathrm{R_f}$: $\mathrm{I(CF_2)_2O(CF_2)_2}$ (**a**), $\mathrm{H(CF_2)_2O(CF_2)_2}$ (**b**), $\mathrm{C_4F_9}$ (**c**). E: P, As.

These reactions proceeded readily in dry benzene or absolute ether at room temperature, and the reaction was monitored by ^{19}F NMR. The chemical shift of $\mathrm{CF_2}$ in the starting material ($-\mathrm{C}F_2\mathrm{SO_2NCl_2}$) is around −106.6 ppm, whereas in the product $-\mathrm{C}F_2\mathrm{SO_2N{=}P}$, it is at −116.6 ppm.

Generally, after stirring for about 5 h, the starting $\mathrm{R_fSO_2NCl_2}$ was all consumed. After removal of the zinc chloride by filtration, the filtrate was evaporated to dryness. The residue was recrystallized from $\mathrm{CH_3CN}$ to give pure product **3** in 72−78% yield. Treatment of **2** with $\mathrm{PBu_3}$ gave a similar result (eq 6).

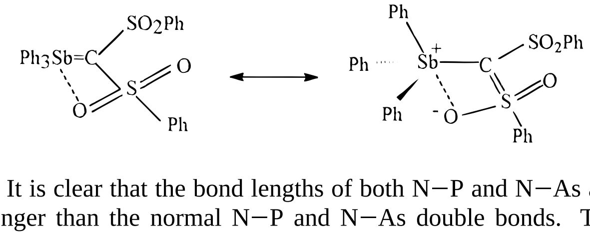
$$\mathrm{PBu_3} + \underset{\mathbf{2}}{\mathrm{I(CF_2)_2O(CF_2)_2SO_2NCl_2}} \xrightarrow[\mathrm{C_6H_6\ or\ Et_2O}]{\mathrm{Zn}} \underset{\mathbf{4}\ (80\%)}{\mathrm{I(CF_2)_2O(CF_2)_2SO_2N{=}PBu_3}} \qquad (6)$$

All of the products (except **4**, which is a colorless liquid) are white solids and stable in dry air (see Table 1).

However, compounds **3** decomposed to the corresponding perfluoroalkanesulfonamides and triphenylphosphine oxide or triphenylarsine oxide when dissolved in solvents such as benzene, ether, and acetonitrile or exposed in air (eq 7).

$$\mathrm{R_fSO_2N{=}EPh_3 + H_2O \xrightarrow[\mathrm{or\ CH_3CN}]{\mathrm{C_6H_6\ or\ Et_2O}} R_fSO_2NH_2 + Ph_3E{=}O} \qquad (7)$$

As monitored by ^{19}F NMR spectroscopy, nearly 60% of **3a** or **3d** decomposed after 24 h. This is similar to the compound $\mathrm{Ph_3Bi{=}NSO_2R_f}$; for this compound the literature[5] gave only elemental analysis, ^{1}H NMR, and ^{19}F NMR. The author pointed out that their ^{13}C NMR spectra could not be obtained because the samples decomposed in solvent during the time required to obtain spectra. Perhaps for the same reason, only the elemental analysis and IR spectrum were given for the compound $\mathrm{CF_3SO_2N{=}SbPh_3}$.[6] In our case both phosphine imine and arsine imine could be recrystallized from dry $\mathrm{C_6H_6{-}CH_3CN}$ in a dry-box, and their structures are fully confirmed by microanalysis, IR, MS, ^{1}H NMR, ^{19}F NMR, ^{13}C NMR, and X-ray diffraction analysis. The ^{13}C NMR spectra of **3a** and **3d** were obtained in a dry $\mathrm{N_2}$ atmosphere, and the ^{13}C NMR spectrum of **3d** showed that a small amount of $\mathrm{Ph_3As{=}O}$ is formed during the scanning period. The X-ray structure analyses of **3a** and **3d** are shown in Figures 1 and 2, respectively. From the X-ray diffraction analysis, both the N−P bond (1.609 Å) and the N−As bond (1.772 Å) have single-bond character. Comparing a similar compound, in triphenylstibonium bis(phenylsulfonyl)methylide, $\mathrm{Ph_3Sb{=}C(SO_2Ph)_2}$, the Sb−O distance is 2.844 Å (0.5 Å shorter than the sum of the van der Waals radii), indicating some interaction between the Sb atom and the O atom.[9]



It is clear that the bond lengths of both N−P and N−As are longer than the normal N−P and N−As double bonds. The

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(1) Staudinger, H.; Meyer, J. *Helv. Chim. Acta* **1919**, *2*, 635.
(2) Senning, A. *Acta Chem. Scand.* **1965**, *19*, 1755.
(3) Mann, F. G.; Chaplin, E. J. *J. Chem. Soc.* **1937**, 527.
(4) Radchenko, O. A.; Nazaretyan, V. P.; Yagupolskii, L. M. *Zh. Obshch. Khim.* **1976**, *46*, 565.
(5) Pasenok, S. V.; Kirij, N. V.; Yagupolskii, Y. L.; Nanmann, D.; Tyrra, W. *J. Fluorine Chem.* **1993**, *63*, 179.
(6) Yagupolskii, L. M. *J. Fluorine Chem.* **1987**, *36*, 1.
(7) Yagupolskii, L. M.; Popov, V. I.; Pavlenko, N. V.; Maletina, I. I.; Mironova, A. A.; Gavrilova, R. Yu.; Orda, V. V. *Zh. Org. Khim.* **1986**, *22*, 2169.
(8) Zhu, S. Z *J. Chem. Soc., Perkin Trans. 1* **1994**, 2077.
(9) Ferguson, G.; Lloyd, D. *J. Chem. Res.* **1987**, 32.

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Table 1. Compounds **3** and **4** ($R_fSO_2N{=}EY_3$)

	R_f	EY_3	mp or bp (°C)	yield[a] (%)
3a	$I(CF_2)_2O(CF_2)_2$	PPh_3	88−90	78
3b	C_4F_9	$AsPh_3$	76−78	74
3c	$H(CF_2)_2O(CF_2)_2$	PPh_3	76−78	72
3d	$I(CF_2)_2O(CF_2)_2$	$AsPh_3$	114−116	77
4	$I(CF_2)_2O(CF_2)_2$	PBu_3	130/2 Torr	80

[a] Yields based on **2**.

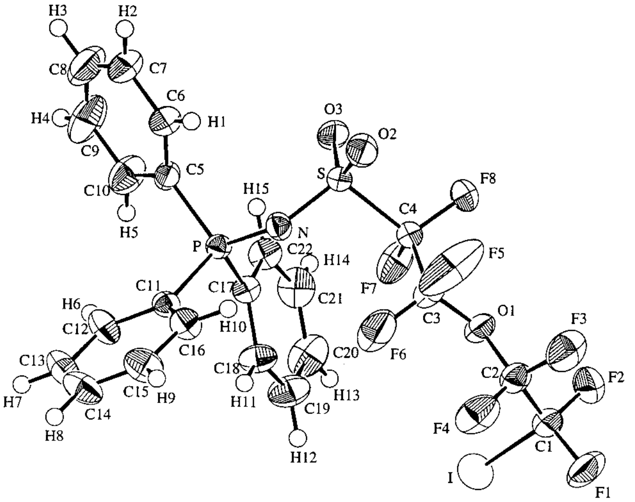


Figure 1. ORTEP drawing of $R_fSO_2N{=}PPh_3$. Selected bond lengths (Å) and bond angles (deg): S−O(2), 1.421; S−O(3), 1.483; S−N, 1.543; P−N, 1.609; N−S−C(4), 105.3; S−N−P 128.9.

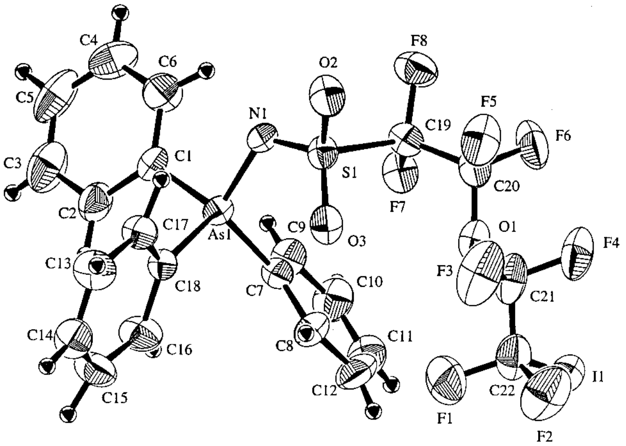
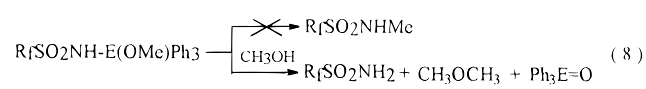


Figure 2. ORTEP drawing of $R_fSO_2N{=}AsPh_3$. Selected bond lengths (Å) and bond angles (deg): S−O(2), 1.437; S−O(3), 1.424; S−N, 1.546; As−N, 1.772; N−S−C(19), 104.5; S−N−As, 119.4.

distances between the P and O atoms (in compound **3a**) and between the As and O atoms (in compound **3d**) are 3.19 and 3.95 Å, and 3.05 and 4.04 Å, respectively; all are longer than the sum of the radii of the P atom (1.06 Å) or the As atom (1.20 Å) and O atom (0.73 Å). (See Tables 2 and Table 3). These data showed that no similar interaction occurred between P−O and As−O in compound **3**.

As mentioned above, **3** are easily hydrolyzed to the corresponding $R_fSO_2NH_2$ and $Ph_3E{=}O$. However, when **3** are treated with methanol, the product is not the expected R_fSO_2NHMe (eq 8).



$$R_fSO_2N{=}EPh_3 \xrightarrow{CH_3OH} R_fSO_2NH\text{-}E(OMe)Ph_3 \begin{cases} \not\longrightarrow R_fSO_2NHMe \\ \xrightarrow{CH_3OH} R_fSO_2NH_2 + CH_3OCH_3 + Ph_3E{=}O \end{cases} \qquad (8)$$

Table 2. Crystallographic Data for the Structure Study of $ICF_2CF_2OCF_2CF_2SO_2N{=}PPh_3$, **3a** and $ICF_2CF_2OCF_2CF_2SO_2N{=}AsPh_3$ **3d**

	3a	**3d**
formula	$C_{22}H_{15}F_8INO_3PS$	$C_{22}H_{15}AsF_8INO_3S$
fw	683.29	727.24
Z	2	4
D(calcd) g/cm^3	1.792	1.873
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a (Å)	10.797(3)	14.800(5)
b (Å)	14.412(2)	9.348(3)
c (Å)	9.328(2)	19.091(2)
α (deg)	99.53(2)	
β (deg)	111.90	102.44(2)
γ (deg)	102.37	
V (Å^3)	1266.4(5)	2579(1)
λ(Mo Kα) (Å)	0.710 69	0.710 69
F(000)	668.00	1408.00
temp (°C)	20.0	20.0
R^a	0.036	0.039
$R_w{}^a$	0.055	0.050
μ(Mo Kα) (cm^{-1})	14.95	26.80

[a] $R = F_0 - F_c/F_o$; $R_w = [(F_o - F_c)^2/wF_o{}^2]^{1/2}$.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for **3a** and **3d**

3a		**3d**	
	Bond Distances		
P(1)−N(1)	1.609(3)	As(1)−N(1)	1.772(5)
P(1)−C(5)	1.792(4)	As(1)−C(1)	1.915(6)
P(1)−C(11)	1.804(4)	As(1)−C(7)	1.908(6)
P(1)−C(17)	1.795(3)	As(1)−C(18)	1.908(7)
N(1)−S(1)	1.543(3)	N(1)−S(1)	1.546(6)
S(1)−O(2)	1.421(3)	S(1)−O(2)	1.437(5)
S(1)−O(3)	1.438(3)	S(1)−O(1)	1.424(5)
	Bond Angles		
C(5)−P(1)−C(11)	108.1(2)	C(1)−As(1)−N(1)	102.5(3)
C(11)−P(1)−C(17)	108.1(2)	C(18)−As(1)−C(7)	109.6(3)
C(17)−P(1)−N(1)	114.2(2)	C(7)−As(1)−N(1)	115.8(3)
C(17)−P(1)−C(5)	109.6(2)	C(1)−As(1)−C(18)	107.4(3)
O(2)−S(1)−N(1)	110.5(2)	O(2)−S(1)−N(1)	110.4(3)
O(3)−S(1)−N(1)	115.2(2)	O(3)−S(1)−N(1)	114.5(3)
S(1)−N(1)−P(1)	128.9(2)	S(1)−N(1)−As(1)	119.4(3)

The (fluoroalkyl)sulfonyl-substituted triphenylphosphine imine $R_fCH_2CH_2N{=}PPh_3$ reacted with CS_2 at normal temperature to give $R_fSO_2N{=}C{=}S$.[10] But in our case, compounds **3** were stable when refluxed in excess CS_2 or reacted in a sealed tube. The reason may due to the strong electron-withdrawing group $R_fSO_2{-}$, which decreased the negative charge on the N atom and reduced its reactivity.

Further chemical translations of these compounds **3** are now under investigation.

Experimental Section

The melting and boiling points reported are uncorrected. Solvents were purified and dried before use. ^1H NMR (60 MHz) and ^{13}C NMR and ^{19}F NMR (54.6 MHz) spectra were recorded on a Varian-360L instrument or a Bruker AM-300 spectrometer with TMS or TFA ($\delta_{CFCl3} = \delta_{TFA} + 76.6$, and with upfield negative) as an internal or external standard, respectively. X-ray structure analysis were performed on a Rigaku AFC7R diffractometer. IR spectra were obtained with an IR-440 Shimadzu spectrophotometer. Lower resolution mass spectra were obtained on a Finnigan GC-MS 4021 instrument.

Preparation of *N*-(Perfluoroalkyl)sulfonyl-Substituted Triphenylphosphine Imine and Arsine Imine. *N,N*-Dichloroperfluoroalkane-

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[10] Trabelsi, E.; Bollens, E.; Jouani, M. A.; Gaysinki, M.; Szoenyi, F.; Cambon, A. *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *90 (*1−4), 185.

sulfonamide **2a** (2.4 g, 4.89 mmol) was added dropwise into a 25 mL flask containing a solution of triphenylphosphine (1.3 g, 4.96 mmol) and benzene (10 mL) in the presence of zinc powder (0.4 g, 6.15 mmol) at room temperature. After 0.5 h of stirring, zinc chloride was filtered out and the filtrate was evaporated to dryness. The crude product was recrystallized from dry CH_3CN (10 mL) at room temperature to give pure **3a** (2.6 g, yield 78%). Similarly, compounds **3b**−**d** were prepared.

$I(CF_2)_2O(CF_2)_2SO_2N{=}PPh_3$, 3a. δ_H (ppm) ($CDCl_3$, TMS): 7.13 (m, C_6H_5). δ_F (ppm): −65.6 (ICF_2, s), −81.1 (OCF_2, m), −84.9 (CF_2O, s), −116.9 (CF_2S, s). δ_C (ppm): 133.6 (d, 4-C, $^4J_{P-C} = 3$ Hz), 133.2 (d, 2-C, $^2J_{P-C} = 11$ Hz), 129.1 (d, 3-C, $^3J_{P-C} = 13$ Hz), 126.3 (d, 1-C, $^1J_{P-C} = 105$ Hz), 116.9 (tt, CF_2), 114.9 (tt, CF_2), 112.1 (tt, CF_2), 89.6 (tt, ICF_2) ($^1J_{F-C} = 320$ Hz, $^2J_{F-C} = 42$ Hz). MS (*m*/*e*, %): 684 (M^+H, 0.63), 683 (M^+, 0.40), 600 ($M^+ - C_6H_5 - O$, 0.50), 556 ($M^+ - I$, 2.03), 341 ($M^+H - IR_f$, 28.48), 340 ($Ph_3PNSO_2^+$, 100.00), 324 (Ph_3PNSO^+, 5.35), 277 ($IC_2F_4^+$, 2.69), 262 (Ph_3P^+, 0.66), 122 ($PhPN^+$, 5.86).

$C_4F_9SO_2N{=}AsPh_3$, 3b. δ_H (ppm) ($CDCl_3$, TMS): 7.50 (m, C_6H_5). δ_F (ppm): −81.1 (CF_3, s), −103.1 (CF_2, t), −121.3 (CF_2, s), −126.3 (CF_2, s). MS (*m*/*e*, %): 604 (M^+H, 0.48), 584 ($M^+ - F$, 0.51), 520 ($M^+ - F - SO_2$, 0.54), 385 ($M^+H - C_4F_9$, 21.14), 384 ($M^+ - C_4F_9$, 100.00), 368 ($M^+ - C_4F_9 - O$, 3.08), 306 ($AsPh_3^+$, 0.84), 229 ($AsPh_2^+$, 5.86), 154 ($2Ph^+$, 9.52), 152 ($AsPh^+$, 25.39), 80 (SO_3^+, 26.56), 69 (CF_3^+, 20.31), 64 (SO_2^+, 9.13). Elemental anal. for $C_{22}H_{15}AsF_9NO_2S$. Required: C, 43.78; H, 2.49; N, 2.32. Found: C, 43.49; H, 2.35; N, 2.32.

$H(CF_2)_2O(CF_2)_2SO_2N{=}PPh_3$, 3c. δ_H (ppm) ($CDCl_3$, TMS): 7.35 (m, C_6H_5), 5.90 (t, HCF_2). δ_F (ppm): −80.6 (OCF_2, t), −88.4 (CF_2O, s), −116.6 (SCF_2, s), −127.6 (HCF_2, d). MS (*m*/*e*, %): 558 (M^+H, 1.61), 538 ($M^+ - F$, 0.50), 277 ($M^+ - R_fSO_2$, 100.00), 341 ($M^+ - R_f$, 11.07), 340 ($M^+ - HR_f$, 48.96), 324 ($M^+ - HR_f - O$, 2.80), 262 (PPh_3^+, 0.83), 201 ($HC_4F_8^+$, 27.50), 185 (PPh_2^+, 7.59), 154 ($2Ph^+$, 5.82), 119 ($C_2F_5^+$, 10.37), 108 (PPh^+, 1.23), 101 ($HC_2F_4^+$, 18.75). Elemental anal. for $C_{22}H_{16}F_8NO_3PS$. Required: C, 47.40; H, 2.87; N, 2.51. Found: C, 47.13; H, 2.55; N, 2.31.

$I(CF_2)_2O(CF_2)_2SO_2N{=}AsPh_3$, 3d. δ_H (ppm) ($CDCl_3$, TMS): 7.60 (m, C_6H_5). δ_F (ppm): −63.2 (ICF_2, s), −80.2 (OCF_2, m), −84.4 (CF_2O, s), −114.9 (CF_2S, s). δ_C (ppm): 132.7 (s, 4-C), 132.3 (s, 2-C), 129.9 (s, 3-C), 127.4 (s, 1-C), 116.9 (tt, CF_2), 114.9 (tt, CF_2), 112.1 (tt, CF_2), 89.6 (tt, ICF_2) ($^1J_{F-C} = 320$ Hz, $^2J_{F-C} = 42$ Hz). MS (*m*/*e*, %): 728 (M^+H, 0.36), 600 ($M^+ - I$, 1.13), 572 ($M^+H - 2 \times Ph$, 0.2), 511 ($M^+ - R_f$, 0.3), 385 ($M^+H - IR_f$, 23.01), 384 ($M^+ - IR_f$, 100.00), 306 ($AsPh_3^+$, 0.96), 227 ($IC_2F_4^+$, 20.39), 177 (ICF_2^+, 3.59), 154 ($2 \times Ph^+$, 7.86), 64 (SO_2^+, 9.34).

$I(CF_2)_2O(CF_2)_2SO_2N{=}PBu_3$, 4. δ_H (ppm) ($CDCl_3$, TMS): 1.0 ($3 \times CH_3$, m), 1.6 ($9 \times CH_2$, m). δ_F (ppm): −64.6 (ICF_2, s), −79.6 (OCF_2, s), −83.6 (CF_2O, s), −114.6 (CF_2S, s). MS (*m*/*e*, %): 624 (M^+H, 20.69), 594 ($M^+ - C_2H_5$, 8.98), 552 ($M^+ - C_5H_{11}$, 5.39), 497 ($M^+H - I$, 21.35), 440 ($M^+H - I - Bu$, 15.21), 412 ($M^+H - I - C_6H_{13}$, 2.79), 280 ($^+N{=}PBu_3$, 100.00), 227 ($IC_2F_4^+$, 31.63), 219 ($C_4F_9^+$, 51.06), 88 (PBu^+, 2.32), 80(SO_3^+, 42.18), 64 (SO_2^+, 57.50), 57 (Bu^+, 6.72). Elemental anal. for $C_{16}H_{27}F_8INO_3PS$. Required: C, 30.82; H, 4.33; N, 2.25. Found: C, 30.51; H, 4.56; N, 2.30.

Reaction of 3a with CS_2. Method A. To a 10 mL flask containing **3a** (1.5 g, 2.2 mmol) was added excess CS_2 in one portion. After 2 days of refluxing, excess CS_2 was removed. The residue was detected by MS and NMR as starting material. **Method B.** The mixture of **3** and excess CS_2 sealed in a tube was heated to 80 °C for 2 days. After removal of the excess CS_2, the starting material was recovered.

Reaction of 3a with Methanol. Stirring a mixture of **3a** (1.5 g, 2.2 mmol) and anhydrous methanol (5 mL) in a 10 mL flask at 80 °C for 8 h gave the corresponding $R_fSO_2NH_2$ (0.88 g, 95%) and $P(O)Ph_3$. The evolved gas was determined by GC−MS to be CH_3OCH_3.

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Supporting Information Available: Tables of crystal data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, torsion angles, and least squares planes of compound **3a** (15 pages). Ordering information is given on any current masthead page.

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