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A convenient route to *N*-perfluoroalkanesulfonyl, *N'*-phenyldiazene *N'*-oxide $R_fSO_2N{=}N^+(O)^-Ph$

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Abstract

A synthesis of *N*-perfluoroalkanesulfonyl-*N'*-phenyldiazene, *N'*-oxides in fair to good yields is described by condensation of nitrosobenzene and *N,N*-dichloroperfluoroalkanesulfonyl amide without promoters.

Keywords: *N,N*-dichloroperfluoroalkanesulfonylamines; Condensation; Azoxy compounds

1. Introduction

Azoxy compounds are of special interest because of their utilization in liquid crystal systems [1–3], polarising plates [4] and blowing agents [5]. Particularly, unsymmetrically occurring azoxy compounds invariably show potent physiological properties [6–10].

There is a growing interest in the preparation of azoxy compounds, involving: 1) Peracetic acid oxidation of diazo compounds [11,12]; 2) Reduction of aromatic nitro compounds using reductants such as zinc, samarium, thallium [13–19]; 3) Treatment of diimide N-oxide derivatives with Grignard reagents [20]; 4) Alkylation of diazotates with either trialkyloxonium tetrafluoroborate or alkyliodides [21]; 5) Reaction of amino derivatives and [(diacetoxy)iodo] benzene in the presence of nitroso compounds [22]. However, these methods are not regiospecific or require hazardous or difficulty accessible starting materials and some are easy to polymerize during the reaction.

Kovacic et al. [23–25] and Lauk'yanov et al. [26] reported a novel synthetic method by treatment of *N,N*-dihaloamines with nitrosoarenes but alkaline conditions or promoters were necessary. For the fluoroazoxy compounds, the literature synthesis is limited to using some lower boiling point agents such as CF_3NO [27–29]. By using the Kovacic condensation reaction, Banks et al. [30] prepared the azoxy-compounds $Py_FN{=}N^+(O)^-Ar$. However, in the absence of a promoter, 4-(dichloroamino)tetrafluoropyridine attacked 2-methyl-nitrosobenzene in acetonitrile to give the corresponding azoxy-compound only in 16% yield.

Considerable attention has been given to the preparation and reactions of *N,N*-dichloroperfluoroalkanesulfonylamines $R_fSO_2NCl_2$ in our laboratory [31]. They were conveniently prepared by one-pot reactions of perfluoroalkanesulfonylamines with KOH (aq.) and chlorine gas. In continuation of our systematic investigation on *N,N*-dichloroperfluoroalkanesulfonyl amines [32,33], we herein report a new convenient method to prepare fluorine-containing azoxy compounds. A series of $R_fSO_2N{=}N^+(O)^-Ph$ were obtained in fair to good yields by treatment of $R_fSO_2NCl_2$ with nitrosobenzene in CH_3CN.

$$\underset{\mathbf{1}}{R_fSO_2NCl_2} + \underset{\mathbf{2}}{PhNO} \xrightarrow[8^\circ C - - RT]{CH_3CN,\ 6\ h} \underset{\mathbf{3}}{R_fSO_2N{=}N^+(O)^-Ph}$$

R_f: $I(CF_2)_2O(CF_2)_2$ (a); $Cl(CF_2)_2O(CF_2)_2$ (b); $H(CF_2)_2O(CF_2)_2$ (c); *n*-C_4F_9 (d); *n*-C_6F_{13} (e); *n*-C_8F_{17} (f).

In this reaction low reaction temperature and the use of a polar solvent can improve the procedure. The products **3(a–c)** are viscous liquid and the compounds **3(d–f)** are solids. All have aromatic odours and can dissolve in both polar and nonpolar solvents, such as CH_3OH, CH_3CN and CCl_4. They darken in colour on standing in air for several days (Table 1).

The infrared spectra in all cases for compounds **3** exhibited strong absorption at 1500 cm^{-1} (N=N) and 1400 cm^{-1} (N=O).

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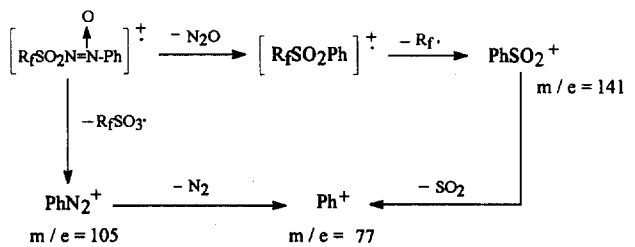
Table 1
Compounds **3** prepared

Entry	Compound		M.p.	Yield[a]
	R_f	**3**	(°C)	(%)
1	$ICF_2CF_2OCF_2CF_2$	**3a**	oil	65
2	$ClCF_2CF_2OCF_2CF_2$	**3b**	oil	58
3	$HCF_2CF_2OCF_2CF_2$	**3c**	oil	63
4	n-C_4F_9	**3d**	38	56
5	n-C_6F_{13}	**3e**	59–61	80
6	n-C_8F_{17}	**3f**	79–81	56

[a]Isolated yields based on **1**.



Scheme 1.

In general, the position of the N–O in the azoxy moiety can be determined by examining the mass spectra of these compound. The most prominent fragmentation process occurs by cleaving the C–N bond to the N-oxide group with the charge mainly retained in the aromatic system which is free from the azoxy-containing portion [34]. In the mass spectra of compounds **3**, all show a strong $M^+ + 1$ peak. The base peak ($m/e = 77$) is determined as Ph^+ which can be derived from $PhSO_2^+$ or PhN_2^+. The fragmentation of $[R_fSO_2Ph]^+$ which would continue from fragmentation of $PhSO_2^+$ peak by cleaving R_f appears in **3(a–d)**, but were notably absent in compound **3(e–f)**. The reason may due to the long chain perfluoroalkyl group. The mass spectra results above can be summarized as shown in Scheme 1.

There are two isomers for azoxy compounds, generally, the *trans*-isomer is more stable than the *cis*-isomer. Considering the NMR spectra, the protons of a *trans*-isomer will be located more downfield than those of the corresponding *cis*-isomer and the most dramatic shifts are seen in the *ortho* protons of the phenyl substituent [35]. For products **3**, the chemical shifts of *ortho* protons occur at δ 7.96–8.20 ppm, whereas the *meta* and *para* protons resonate at δ 7.40–7.75 ppm. When **3d** was heated to 180°C, no changes occurred in the NMR spectra. According to that, we can propose that **3** are formed as *trans*-isomers.

Kovacic et al. [23–25] and Lauk'yanov et al. [26] noted that the addition of promoters, such as KOH, CuCl, $CuBr_2$, could improve the reaction. However, in our cases, such procedures are impractical. It is concluded from ESR studies that the reaction may involve a radical mechanism [36].

2. Experimental

Mps. reported are uncorrected. Solvents were purified and dried before use. ^1H NMR (60 MHz) and ^{19}F NMR (54.6 MHz) spectra were recorded on a Varian-360L instrument or a Bruker AM-300 spectrometer with TMS and TFA ($\delta_{CFCl_3} = \delta_{TFA} + 76.6$ ppm, and with upfield positive) as internal and external standards, respectively. IR spectra were obtained with IR-440 Shimadzu or Perkin-Elmer 983 G spectrophotometers. Low resolution mass spectra were obtained on a Finnigan GC-MS 4021.

2.1. General procedure

A solution of nitrosobenzene **2** (0.62 g, 5.7 mmol) in CH_3CN was cooled with stirring to 0°C. **1a** (2.1 g, 5.7 mmol) was added dropwise in nitrogen gas with the reaction temperature lower than 8°C. Then the mixture was allowed to warm to room temperature for 6 h. After removing the solvent by rotary evaporation, the azoxy compound was afforded as a dark oil. Column chromatography on silica gel with ethyl acetate/petroleum ether (1:6.5) gave **3a** (1.46 g, 63%).

$ICF_2CF_2OCF_2CF_2SO_2N{=}N^+(O)^-C_6H_5$ **3a** ^1H NMR ($CDCl_3$) δ(ppm): 7.40–7.75 (3ArH, m), 7.96–8.20 (2ArH, m). ^{19}F NMR δ(ppm): −12.6 (ICF_2, s), 3.6(OCF_2, t), 8.0(CF_2O, m), 37.6(SO_2CF_2, s). IR (ν_{max}, cm^{-1}): 1590 (w), 1490 (s), 1440 (s), 1380 (s), 1300 (s), 1220–1100 (vs), 980 (m), 910 (s), 780 (s), 710 (m), 690 (s), 670 (s). MS (m/e, %): 529 (M^+H, 6.61), 401 ($M^+ - I$, 7.77), 484 ($M^+ - N_2O$, 0.44), 227 ($ICF_2CF_2^+$, 6.80), 141 ($M^+ - ICF_2CF_2OCF_2CF_2 - N_2O$ or $C_6H_5SO_2^+$, 49.81), 185 ($M^+ - ICF_2CF_2OCF_2CF_2$, 0.33), 105 ($C_6H_5N_2^+$, 70.44), 119 ($C_2F_5^+$, 6.13), 77 ($C_6H_5^+$, 100.00), 93($HSO_2N_2^+$, 40.4). Analysis for $C_{10}H_5F_8N_2O_4SI$: Required: C, 22.74; H, 0.99; N, 5.31; F, 28.79%. Found: C, 23.23; H, 0.99; N, 5.59; F, 29.12%.

$ClCF_2CF_2OCF_2CF_2SO_2N{=}N^+(O)^-C_6H_5$ **3b** ^1H NMR ($CDCl_3$) δ(ppm): 7.36–7.67 (3ArH, m), 8.0–8.14 (2ArH, m). ^{19}F NMR δ(ppm): −4.0 ($ClCF_2$, s), 3.5 (OCF_2, t), 9.2(CF_2O, m), 38.5(SO_2CF_2, s). IR (ν_{max}, cm^{-1}): 2924 (w), 1586 (w), 1446 (m), 1438 (s), 1392 (s), 1352 (s), 1307 (s), 1240–1120 (vs), 975 (m), 905 (w), 785 (m), 701 (m), 688 (s), 638 (s). MS (m/e, %): 439/437 ($M^+(^{37}Cl) + 1/M^+(^{35}Cl) + 1$, 1.56/4.06), 401 ($M^+ - Cl$, 0.51), 392 ($M^+ - N_2O$, 0.21), 141 ($M^+ - ClCF_2CF_2OCF_2CF_2 - N_2O$ or $C_6H_5SO_2^+$, 27.50), 135 ($ClCF_2CF_2^+$, 6.80), 105 ($C_6H_5N_2^+$, 33.57), 93 ($HSO_2N_2^+$, 22.66), 77($C_6H_5^+$, 100.00). Analysis for $C_{10}H_5F_8N_2O_4SCl$: Required: C, 27.57; H, 1.15; N, 6.41%. Found: C, 28.31; H, 1.04; N, 5.64%.

$HCF_2CF_2OCF_2CF_2SO_2N{=}N^+(O)^-C_6H_5$ **3c** ^1H NMR ($CDCl_3$) δ(ppm): 5.86 (HCF_2, t–t, $J_{HF} = 51.6$ Hz), 7.48–7.73 (3ArH, m), 8.03–8.16 (2ArH, m). ^{19}F NMR δ(ppm): 3.4 (OCF_2, t), 11.0 (CF_2O, m), 38.0 (SO_2CF_2, s), 60.4 (HCF_2, d). IR (ν_{max}, cm^{-1}): 2924 (w), 1586 (w), 1490 (m), 1450 (s), 1392 (s), 1352 (s), 1307 (s), 1240–1120

(vs), 975 (m), 905 (w), 785 (m), 701 (m), 688 (s), 638 (s). MS (*m/e*, %): 403 (M^+H, 8.79), 383 ($M^+ - F$, 0.29), 358 ($M^+ - N_2O$, 0.26),185 ($M^+ - HCF_2CF_2OCF_2CF_2$, 0.21), 141 ($M^+ - HCF_2CF_2OCF_2CF_2 - N_2O$ or $C_6H_5SO_2^+$, 27.50), 119 ($C_2F_5^+$, 12.77), 105 ($C_6H_5N_2^+$, 29.60), 101 ($HC_2F_4^+$, 13.32), 77 ($C_6H_5^+$, 100.00), 93 ($HSO_2N_2^+$, 22.66), 64 (SO_2^+, 2.12), 51($C_4H_3^+$, 27.47). Analysis for $C_{10}H_6F_8N_2O_4S$: Required: C, 29.86; H, 1.50; N, 6.97; F, 37.79%. Found: C, 29.79; H, 1.46; N, 6.97; F, 37.79%.

n-$C_4F_9SO_2N{=}N^+(O)^-C_6H_5$ **3d** ^1H NMR ($CDCl_3$) δ (ppm): 7.45–7.88 (3ArH, m), 8.05–8.28 (2ArH, m). ^{19}F NMR δ (ppm): 3.6 (CF_3, s), 34.8 (SO_2CF_2, t), 43.3 (CF_2, s), 48.6 (CF_2, t). IR (ν_{max}, cm^{-1}): 2903 (w), 1590 (w), 1492 (s), 1440 (m), 1390 (s), 1350 (m), 1310 (s), 1260–1170 (vs), 1140 (s), 800 (m), 780 (m), 730 (s), 690 (s). MS (*m/e*, %): 405 (M^+H, 0.93), 360 ($M^+ - N_2O$, 0.14), 219($C_4F_9^+$, 2.57), 185 ($M^+ - C_4F_9$, 0.66), 141 ($M^+ - C_4F_9 - N_2O$ or $C_6H_5SO_2^+$, 27.50), 169 ($C_3F_7^+$, 0.74), 121 ($C_6H_5N_2O^+$, 0.12), 119 ($C_2F_5^+$, 12.77), 107 ($C_6H_5NO^+$, 5.05), 105 ($C_6H_5N_2^+$, 4.12), 101 ($HC_2F_4^+$, 13.32), 77 ($C_6H_5^+$, 100.00), 93 ($HSO_2N_2^+$, 40.4). Analysis for $C_{10}H_5F_9N_2O_3S$: Required: C, 29.70; H, 1.21; N, 6.93%. Found: C, 29.75; H, 0.92; N, 6.77%.

n-$C_6F_{13}SO_2N{=}N^+(O)^-C_6H_5$ **3e** ^1H NMR ($CDCl_3$) δ (ppm): 7.40–7.70 (3ArH, m), 8.05–8.13 (2ArH, m). ^{19}F NMR δ (ppm): 4.0 (CF_3, s), 34.8 (SO_2CF_2, t), 42.7 (CF_2, s), 44.5 (CF_2, s), 45.3 (CF_2, s), 49.0 (CF_2, s). IR (ν_{max}, cm^{-1}): 2903 (w), 1487 (s), 1442 (m), 1390 (s), 1321 (s), 1243–1152 (vs), 1053 (m), 1027 (m), 989 (m), 914 (m), 799 (m), 668 (s), 641 (w). MS (*m/e*, %): 505 (M^+H, 4.89), 185 ($M^+ - C_6F_{13}$, 0.34), 169 ($C_3F_7^+$, 14.92), 141 ($M^+ - C_6F_{13} - N_2O$ or $C_6H_5SO_2^+$, 30.27), 119 ($C_2F_5^+$, 13.52), 108 ($SO_2N_2O^+$, 1.45), 105 ($C_6H_5N_2^+$, 4.12), 101 ($HC_2F_4^+$, 13.32), 93 ($HSO_2N_2^+$, 57.86), 77 ($C_6H_5^+$, 100.00), 69 (CF_3^+, 23.11), 51 ($C_4H_3^+$, 38.38) Analysis for $C_{10}H_5F_{13}N_2O_3S$: Required: C, 28.58; H, 0.99; N, 5.56%. Found: C, 28.62; H, 0.82; N, 5.50%.

n-$C_8F_{17}SO_2N{=}N^+(O)^-C_6H_5$ **3f** ^1H NMR ($CDCl_3$) δ (ppm): 7.55–7.93 (3ArH, m), 8.10–8.35 (2ArH, s). ^{19}F NMR δ (ppm): 3.3 (CF_3, s), 34.3 (SO_2CF_2, t), 42.2 (CF_2, s), 44.0 ($3\times CF_2$, br), 45.0 (CF_2, s), 48.5 (CF_2, s). IR (ν_{max}, cm^{-1}): 2903 (w), 1490 (s), 1450 (m), 1380 (s), 1330 (s), 1320 (m), 1250–1150 (vs), 790 (m), 780 (m), 700 (s), 660 (m), 540 (m). MS (*m/e*, %): 605 (M^+H, 2.37), 521 ($M^+ - F - SO_2$, 0.30), 419 ($C_8F_{17}^+$, 0.20), 219 ($C_4F_9^+$, 2.22), 185 ($M^+ - C_8F_{17}$, 0.26), 169 ($C_3F_7^+$, 8.37), 141($M^+ - C_8F_{17} - N_2O$ or $C_6H_5SO_2^+$, 14.26), 119 ($C_2F_5^+$, 7.27), 105 ($C_6H_5N_2^+$, 13.87), 77($C_6H_5^+$, 100.00), 69 (CF_3^+, 17.80), 51 ($C_4H_3^+$, 20.89). Analysis for $C_{14}H_5F_{17}N_2O_3S$: Required: C, 27.83; H, 0.83; N, 4.64%. Found: C, 28.32; H, 0.86; N, 4.72%.

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References

[1] W.H. De Jeu, W.J.A. Goossens, J. Chem. Phys. 61 (1974) 1985.
[2] J. Van der Veen, W.H. De deu, M.W.M. Wanninkhof, C.A.M. Tienhoven, J. Phys. Chem. 77 (1973) 2153.
[3] A.V. Reiter, V.P. Sevostyanov, O.V. Petrova, Zavod lab. 47 (1981) 20 [CA:94:219079g].
[4] T. Muto, Jpn. Kokai Tokkyo Koho Jp. 08,136,914. [CA, 125: 127987g].
[5] R.E. MacLeay, US 4,228,069. [CA, 94: 66734q].
[6] N. Nishida, A. Kobayashi, T. Nagahama, Bull. Agr. Chem. Soc. Jp. 17 (1955) 77.
[7] B. Korsch, N.V. Riggs, Tetrahedron Lett., (1964) 523.
[8] C.L. Stevens, B.T. Gillis, T.H. Haskell, J. Am. Chem. Soc. 81 (1959) 1435.
[9] W.J. McGahren, M.P. Kunstmann, J. Am. Chem. Soc. 91 (1969) 2808.
[10] A. Gasco, A. Serafino, V. Mortarini, E. Menziani, Tetrahedron Lett., (1964) 3431.
[11] S.V. Blokhina, G.G. Maidachenko, L.I. Minegv, V.I. Klopov, Zh. Org. Khim. 17 (1) (1981) 151.
[12] R.E. Banks, Y. Djebli, R. Fields, N.O. Olawore, R.G. Pritchard, E. Tsiliopoulos, J. Chem. Soc. Perkin Trans I (1989) 1117.
[13] S. Oae, T. Fukumoto, M. Yamagami, Bull. Chem. Soc. Jpn. 36 (1963) 728.
[14] K. Ohe, S. Uemura, N. Sugita, T. Masuda, J. Org. Chem. 54 (1989) 4169.
[15] S.A. Buckler, L. Doll, F.K. Lind, M. Epstein, J. Org. Chem. 27 (1962) 794.
[16] B. Baruah, A. Boruah, D. Prajapati, J.S. Sandhu, Chem. Lett. 5 (1996) 351.
[17] A. Mckillop, R.A. Raphael, J. Org. Chem. (1970) 1670.
[18] Y. Muto, M. Kato, H.B. Jonassen, Bull. Chem. Soc. Jpn. (1967) 1535.
[19] Z.M. Hou, Y. Fujwara, H. Taniguchi, J. Org. Chem. 53 (1988) 3118.
[20] T.E. Stevens, J. Org. Chem. 32 (1967) 1641.
[21] R.A. Moss, T.B.K. Lee, J. Chem. Soc. Perkin I, 1973, 2778.
[22] R.M. Moriarty, T.E. Hopkins, I. Prakash, B.K. Vaid, R.K. Vaid, Syn. Comm. 20 (1990) 2353.
[23] F.R. Sullivan, E. Luck, P. Kovacic, J. Org. Chem. 39 (1974) 2967.
[24] V. Nelson, A. Serianz, P. Kovacic, J. Org. Chem. 41 (1976) 1751.
[25] R.C. Zawalski, P. Kovacic, J. Org. Chem. 44 (1979) 2130.
[26] O.A. Lauk'yanov, Yu.B. Salamonov, S.I. Zherebyat'ev, et al., Izv. Akad. Nauk, SSSR, Ser. Khim. 5 (1989) 1110.
[27] T.E. Stevens, J.P. Freeman, J. Org. Chem. 29 (1964) 2279.
[28] R.E. Banks, W.T. Flowers, R.N. Haszeldine, J. Chem. Soc. Perkin Trans I, 1979, 2765.
[29] H. Hope, C.B. Shoemaker, D.P. Shoemaker, H.M. Marsden, J.M. Shreeve, J. Org. Chem. 50 (1985) 1136.
[30] R.E. Banks, I.M. Farhat, R.R. Fields, G. Pritchard, M.M. Saleh, J. Fluorine Chem. 28 (1985) 325.
[31] S.Z. Zhu, J. Chem. Soc. Perkin Trans I, 1994, 2077.
[32] S.Z. Zhu, C.M. Zhou, A.W. Li, B. Xu, J. Fluorine Chem. 67 (1994) 7.
[33] B. Xu, S.Z. Zhu, Heteroatom Chem. 8 (1997) 309.
[34] J.H. Bowie, R.G. Cooks, G.E. Lewis, Aus. J. Chem. 20 (1967) 1601.
[35] K.G. Taylor, T. Riehl, J. Am. Chem. Soc. 94 (1972) 250.
[36] C.M. Zhou, S.Z. Zhu, Y.H. Zhang, B. Xu, J. Zhang, X.K. Jiang, J. Fluorine Chem. 73 (1995) 175.