ELSEVIER

Journal of Fluorine Chemistry 69 (1994) 249–251

JOURNAL OF FLUORINE CHEMISTRY

4,4′-Dichloro- and 4-chloro-4′-hydroxy-2,2′-bis(trifluoromethyl)diphenyl sulphoxides and sulphones

James H. Clark*, James E. Denness, Andrew J. Wynd

Department of Chemistry, University of York, Heslington, York, Y01 5DD, UK

Received 22 July 1993; accepted 9 December 1993

Abstract

4,4′-Dichloro-2,2′-bis(trifluoromethyl)diphenyl sulphoxide can be prepared from 2-bromo-4-chlorobenzotrifluoride and converted to the 2,2′-bis(trifluoromethyl)diphenyl sulphone, although the oxidation is remarkably difficult owing to the steric protection of the lone pair on sulphur by the two CF_3 groups. Both the sulphoxide and the sulphone can be converted into the 4-chloro-4′-hydroxy single monomers.

Keywords: Dichloro-bis(trifluoromethyl)diphenyl sulphoxide; Bis(trifluoromethyl)diphenyl sulphone; NMR spectroscopy; IR spectroscopy; Crystal structure determination; Mass spectrometry

1. Introduction

Functionalised diphenyl sulphones are of importance as monomers for engineering thermoplastics [1] such as PES (PolyEther Sulphone). There is growing interest in the incorporation of fluorine into such high-performance polymers so as to improve their resistance to water, their electrical properties and their processability [2]. As part of our studies in this area we have synthesized the novel sulphone monomers shown in Scheme 1.

2. Results and discussion

The preparation of sulphoxide **1a** is straightforward, although its subsequent oxidation to sulphone **2a** proved to be remarkably difficult. Conventionally [3] sulphoxides are readily oxidised to sulphones using reagents such as nitric acid or hydrogen peroxide/ethanoic acid. Surprisingly, these reagents proved ineffective for the oxidation of **1a** to **2a** (indeed nitric acid proved to be a convenient purification step in the preparation of **1a**), which was eventually accomplished only by heating **1a** with chromium trioxide in ethanoic acid over a long period of time. The ^{19}F NMR spectra of **1a** and **2a** showed the expected singlets ($\delta - 58.8$ and -57.4 ppm, respectively). Preparation of the useful 'single monomers' 4-chloro-4′-hydroxy-2,2′-bis(trifluoromethyl)diphenyl sulphoxide (**1b**) and 4-chloro-4′-hydroxy-2,2′-bis(trifluoromethyl)diphenyl sulphone (**2b**) [4][1] was then readily accomplished by reaction of **1a** and **2a** with potassium hydroxide in aqueous dimethyl sulphoxide at 120 °C. The ^{19}F NMR spectrum of **2b** showed the expected two singlets (δ -56.5 and -56.6 ppm) but that of **1b** unexpectedly showed a pair of quartets (δ -57.8 ppm, $J=5.1$ Hz; δ -57.0 ppm, $J=5.1$ Hz). We were able to assign the splitting as a fluorine–fluorine coupling by ^{19}F (COSY) NMR. This is formally an eight-bond coupling, but the lack of F−F coupling in **2b** led us to believe that it is an unusual example of a through-space coupling presumably brought about by the geometry of **1b** placing the two CF_3 groups in close proximity.

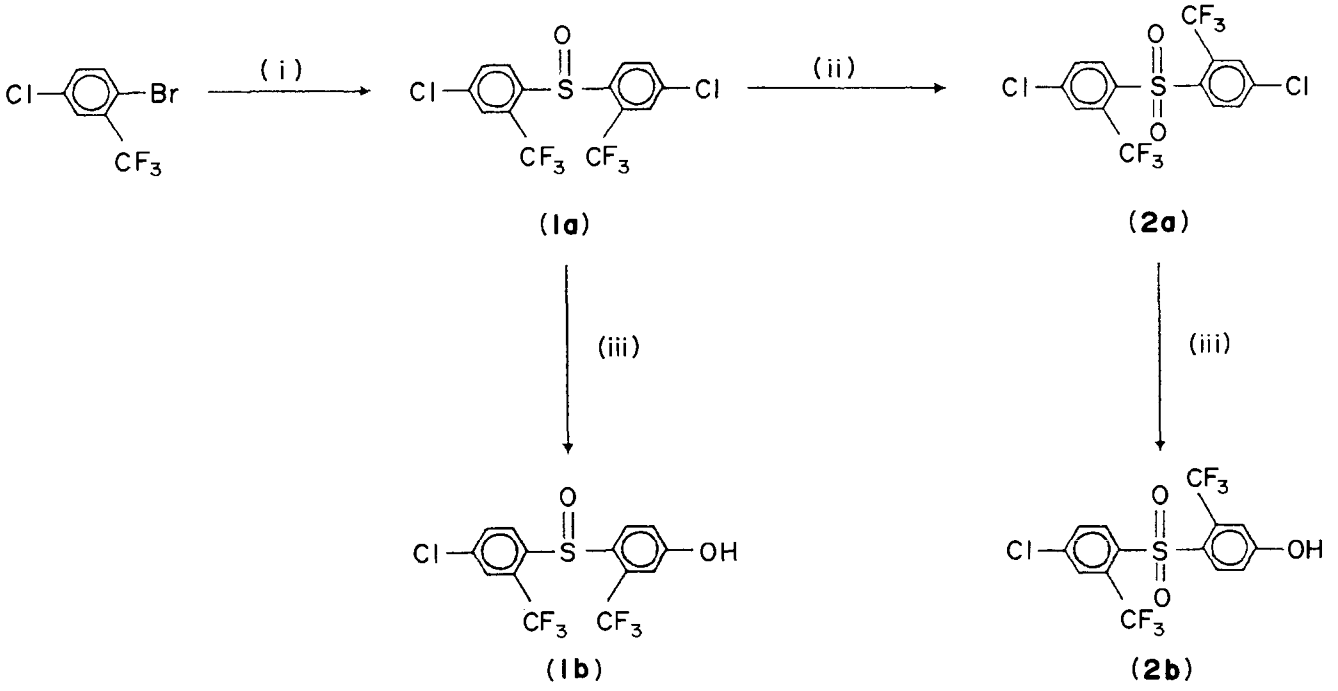
Unfortunately we were unable to obtain crystals of **1b** suitable for X-ray analysis that might enable us to determine its structure. However, suitable crystals of **1a** were obtained, and the resulting X-ray crystallographic analysis did indeed reveal geometrically close CF_3 groups (Fig. 1). The shortest intergroup fluorine–fluorine (271 pm) and fluorine–sulphur (329 pm) distances are close to the respective sums of the van der Waals radii. In contrast, single-crystal X-ray dif-

---

*Corresponding author.

[1] It should also be possible to prepare analogues of symmetrical sulphoxide and sulphone (**1a** and **2a**) by the route shown in Scheme 1 (e.g. the non-chlorinated analogues starting from 2-bromobenzotrifluoride).

SSDI 0022-1139(94)03080-J



Scheme 1. Reaction conditions: (i) ethoxyethane, Mg then (at 0 °C) $SOCl_2$, 19 h, H^+/H_2O; (ii) CrO_3, CH_3CO_2H, 100 °C, 24 h; (iii) KOH (2 mol equiv.) in 85% aqueous DMSO, 120 °C, 5 h, H^+/H_2O.

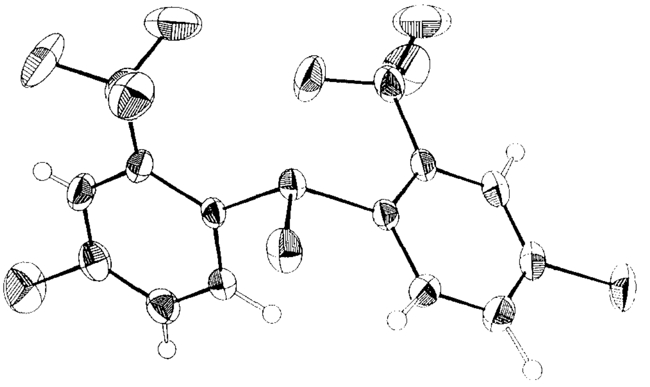


Fig. 1. The molecular structure of compound **1a**. Atoms are drawn with 30% probability ellipsoids except for hydrogen atoms which have an artificial radius of 10 pm.

fraction studies on **2a** showed the CF_3 groups on opposite sides of the molecule consistent with a lack of fluorine–fluorine coupling in **2b**. It is also interesting to note that the 'axial twist' of the rings about the sulphur–carbon bonds reveals considerable asymmetry in **1a** (but not in **2a**) which may be related to overlap between orbitals on the sulphur and the π orbitals on the phenyl ring. Such π interactions will restrict rotation about the sulphur–carbon bonds, and so enable the observed fluorine–fluorine couplings to occur through space. Furthermore, the geometry adopted will afford protection of the lone pair on sulphur by the two CF_3 groups and hence make the molecule less susceptible to oxidation.

3. Experimental details

NMR spectra were obtained on Bruker MSL (^1H, 308.13 MHz; ^{19}F, 282.404 MHz) and JEOL FX90Q (^{19}F, 84.36 MHz) spectrometers using $CDCl_3$ or $(CD_3)_2SO$ solutions. IR spectra were obtained on a PE 1720 FT-IR spectrophotometer. Mass spectra were determined on Kratos MS3074 or VG Autospec instruments.

Crystal data were obtained using an Enraf-Nonius CAD4 diffractometer (λ[Mo Kα] = 71.069 pm). Compound **1a** was grown as colourless plates by slow evaporation of an ethanol solution, while compound **2a** was grown as colourless plates by slow evaporation of a 1:1 dichloromethane/ethoxyethane solution.

$C_{14}H_6Cl_2F_6OS$ (**1a**), M = 407.09; triclinic, space group $P1$, $a = 0.7153(3)$, $b = 0.73021(15)$, $c = 1.6374(3)$ nm, $\alpha = 84.5751(6)$, $\beta = 89.17(2)$, $\gamma = 64.54(2)°$, $U = 0.7684$ nm^3, $Z = 2$, $D_c = 1.759$ mg m^{-3}, μ(Mo Kα) = 616 m^{-1}, $T = 273$ K, $F(000) = 404$. A total of 2366 unique reflections ($\theta_{max} = 25°$) with $|F| > 2\sigma(F)$ were retained and used in the refinement which converged with $R = 0.042$, $R_w = 0.074$ and $S = 1.44$.

$C_{14}H_6Cl_2F_6O_2S$ (**2a**), M = 423.08; monoclinic, space group $P2_1/n$, $a = 0.8906(4)$, $b = 1.8905(5)$, $c = 0.9718(4)$ nm, $\beta = 110.96(4)°$, $U = 1.5279$ nm^3, $Z = 4$, $D_c = 1.839$ mg m^{-3}, μ(Mo Kα) = 627 m^{-1}, $T = 273$ K, $F(000) = 840$. A total of 1912 unique reflections ($\theta_{max} = 25°$) with $|F| > 2\sigma(F)$ were retained and used in the refinement which converged with $R = 0.047$, $R_w = 0.061$ and $S = 1.39$.

For the structure solution and refinement, S, O, Cl and phenyl C atoms were located by automatic direct methods, and the other atoms by subsequent iterative full-matrix least-squares refinement and F syntheses.

3.1. 4,4'-Dichloro-2,2'-bis(trifluoromethyl)diphenyl sulphoxide (1a)

A solution consisting of 101.3 g (0.39 mol) of 2-bromo-5-chlorobenzotrifluoride in 25 ml of ethoxyethane was added over a period of 2 h to a mixture of 9.49 g (0.39 mol) of magnesium turnings and 250 ml of ethoxyethane. Thionyl chloride (14.15 ml, 0.195 mol) in 80 ml of ethoxyethane was then added over 1 h. The mixture was then stirred overnight, heated to reflux for 0.5 h, cooled and treated with 70 ml of 1 M HCl. This gave a brown solid (crude yield, 97%) which was further purified by stirring with concentrated HNO_3 at 100 °C for 21 h. Cooling followed by dilution and extraction with ethoxyethane gave, on evaporation, and recrystallization from ethanol, the sulphoxide as a pale yellow crystalline material in a yield of 15%; m.p. 132–133 °C. Analysis: Calc. for $C_{14}H_6Cl_2F_6OS$: C, 41.3; H, 1.5%. Found: C, 41.4; H, 1.4%. IR ν_{max} (Nujol) (cm^{-1}): 1085 (CF_3); 1065 (S=O). ^1H NMR ($CDCl_3$) δ: 7.72 (2H, dd, J=2.1, 8.4 Hz, 5-H); 7.76 (2H, d, J=2.0 Hz, 3-H); 7.84 (2H, d, J=8.4 Hz) ppm. ^{19}F NMR ($CDCl_3$) δ: −58.81 (s, CF_3) ppm. MS *m/z*: 408 (18); 406 (26); 392 (8); 390 (13); 229 (11); 227 (32); 213 (36); 211 (100).

3.2. 4,4'-Dichloro-2,2'-bis(trifluoromethyl)diphenyl sulphone (2a)

The oxidation was carried out using the brown, crude sulphoxide product described above. This material (77.26 g) was stirred with 70 g (0.7 mol) of chromium trioxide in 650 ml of ethanoic acid at 100 °C for 24 h. Cooling and dilution with water gave a pale green precipitate which was recrystallised from propan-2-ol in the presence of charcoal and Celite to give the sulphone as a white crystalline material in a yield of 59%; m.p. 145.5–146 °C. Analysis: Calc. for $C_{14}H_6Cl_2F_6O_2S$: C, 39.7; H, 1.4; Cl, 16.8%. Found: C, 39.9; H, 1.15; Cl, 17.1%. IR ν_{max} (cm^{-1}): 1303, 1138 (SO_2); 1090 (CF_3). ^1H NMR ($CDCl_3$) δ: 8.32 (2H, d, J=8.6 Hz, 6-H); 7.83 (2H, d, J=2.1 Hz, 3-H); 7.76 (2H, dd, J=2.1 Hz, 8.6 Hz) ppm. ^{19}F NMR ($CDCl_3$) δ: −57.4 (CF_3) ppm.

3.3. 4-Chloro-4'-hydroxy-2,2'-bis(trifluoromethyl)diphenyl sulphoxide (1b)

Compound **1a** (5.20 g, 0.0128 mol) in 110 ml of DMSO was heated to 130 °C and to the solution was added aqueous KOH (1 M, 25 ml, 0.025 mol). The mixture was heated for 1.5 h and then poured into aqueous HCl. The precipitate was filtered off and recrystallised from methanol to give **1b** as colourless needles in a yield of 47%: m.p. 128–130 °C. IR ν_{max} (cm^{-1}): 3180 (OH). ^1H NMR ($CDCl_3$) δ: 9.85 (1H, br., s, Ar*OH*); 8.15 (1H, d, J=9.6 Hz, 6-H); 8.01 (1H, dd, J=2.1 and 8.5 Hz, 5-H); 7.92 (1H, d, J=1.9 Hz, 3-H); 7.62 (1H, d, J=8.7 Hz, 6-H); 7.32 (1H, d, J=2.5 Hz, 3-H); 7.25 (1H, dd, J=2.6 and 8.7 Hz, 5-H) [ring resonances assigned by ^1H(COSY)] ppm. ^{19}F NMR δ: −57.79 (3F, q, J_{FF}=5.1 Hz, CF_3); −56.97 (3F, q, J_{FF}=5.1 Hz, CF_3) ppm. MS *m/z*: 388 (M^+, 22%).

3.4. 4-Chloro-4'-hydroxy-2,2'-bis(trifluoromethyl)diphenyl sulphone (2b)

Compound **2a** (2.98 g, 0.00706 mol) in 85 ml of DMSO was heated to 120 °C and to the solution was added aqueous KOH (1 M, 15 ml, 0.015 mol). The mixture was heated for 5 h and then worked up as above to give, after recrystallisation from aqueous ethanoic acid, **2b** as an off-white solid in a yield of 40%: m.p. 174–177 °C. IR ν_{max} (cm^{-1}): 3190(OH). ^1H NMR δ: 11.60 (1H, br., s, Ar*OH*); 8.13 (1H, d, J=4.1 Hz, 3-H); 8.11 (1H, d, J=6.9 Hz, 6-H); 8.00 (1H, dd, J=2.1 and 8.6 Hz, 5-H); 7.91 (2H, d, J=8.6 Hz, 6-H); 7.37 (1H, d, J=2.5 Hz, 3-H); 7.31 (1H, dd, J=2.5 and 8.9 Hz, 5-H) [ring resonances assigned by ^1H(COSY)] ppm. ^{19}F NMR δ: −56.54 (3F, s, CF_3); −56.59 (3F, s, CF_3) ppm. MS *m/z*: 404 (M^+, 60%).

Acknowledgements

We thank ICI and SERC for financial support; M. Garner and A.S. Piers for NMR spectra; Dr. A.J. Welch for the use of X-ray diffraction facilities and Dr. G.F. Mitchell for assistance with the work on structural comparisons.

References

[1] E.B. Seymour and G.S. Kirshenbaum (eds.), *High Performance Polymers: Their Origin and Development*, Elsevier, New York, 1986.

[2] P.E. Cassidy, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem., 31* (1990) 338; T. Ichino, S. Sasaki, T. Matsura and S. Nishi, *J. Polym. Sci., Part A-1, 28* (1990) 232; F.W. Mercer and T.D. Goodmann, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem., 32* (1991) 189; J.E. McGrath, H. Grubbs, M.E. Rogers, R. Mercier, W.A. Joseph, W. Alton, D. Rodriguez and G.L. Wilkes, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem., 32* (1991) 103; J.W. Labadie and J.L. Hedrick, *Macromolecules, 23* (1990) 5371.

[3] J. Drabowsicz, P. Keilbasuiski and M. Mikolajczyk, in S. Patai, Z. Rappoport and C. Stirling (eds.), *The Chemistry of Sulphones and Sulphoxides — The Chemistry of Functional Group Series*, Wiley Intersciences, Chichester, 1988, Chapter 8.

[4] J.E. Denness, *D. Phil. Thesis*, University of York, 1992.