Reactions involving hexafluoropropylene oxide.[1] Part 2. A novel "dethioesterification" of a fluorinated sulfur containing ester

Paul L. Coe,*[a] Marianne Löhr,[a] Owen R. Chambers[b] and Christophe Rochin[b]

[a] *School of Chemistry, University of Birmingham, Fluorine Laboratories, Edgbaston, Birmingham, UK B15 2TT*
[b] *Rhodia Chemicals, Avonmouth, UK BS11 9YF*

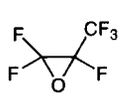
Received (in Cambridge) 14th December 1998, Accepted 20th January 1999

Ring opening reactions of hexafluoropropylene oxide (HFPO) **1** with thiophenol gave the thioesters, **2**, **6** and **7** depending on the conditions used to activate the thiol group. Saponification of the ester **2** led, in a slow reaction, to the acid **3**. In an attempt to improve the saponification of thioester **2** the use of silver nitrate in dioxane–water surprisingly led to the formation of the hydro compound **4** *via* a novel "dethioesterification" reaction. The potential use of the chemistry described for the introduction of fluorinated functions stereospecifically is discussed.

Introduction

Although the building block approach has been applied extensively to the formation of partly fluorinated compounds[2] there have been relatively few examples of the formation and reaction of chiral derivatives.[3a,b] Many of the compounds known have been obtained by chemical or enzymatic resolution *e.g.* from the work of Kitazume and his group.[4] Good examples of the use of chemical resolution to produce chiral products are the reports of Halpern[5] and Rozov[6a] who prepared the enantiomers of the anaesthetics isoflurane and desfluorane. Rozov in particular used hexafluoropropylene oxide as starting material and was able to produce enantiomerically pure desfluorane. A key step in this work was the decarboxylation of resolved 1-methoxytetrafluoropropionic acid which was shown to proceed with retention of configuration.[6b] It seemed possible to us that this could provide a route to sulfur stabilised carbanions generated *in situ* from suitable fluorocarboxylic acids. Further, in the light of our recent work[1] where we presented compelling evidence to suggest that the Reformatsky reaction of ethyl (*S*)-2-bromotetrafluoropropionate proceeded with either complete retention or complete inversion of configuration, we potentially have a route to the direct formation of chiral derivatives *via* sulfur stabilised carbanions.

Entry into a wide range of chiral fluorocarbon precursors comes from reactions of hexafluoropropylene oxide (HFPO) **1**,



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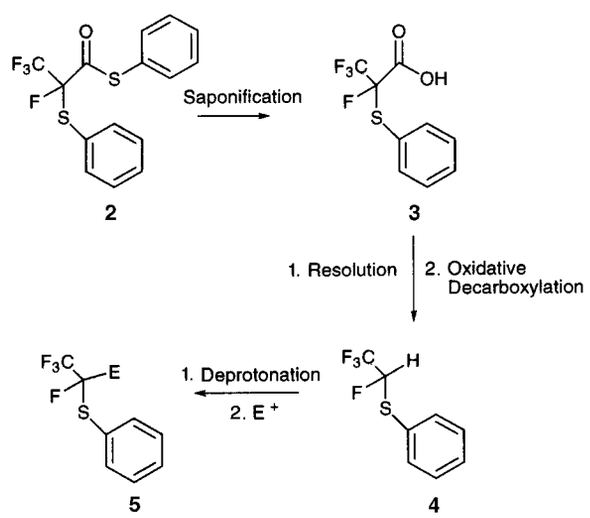
the chemistry of which has been extensively reviewed by Siegemund.[7] We now report further reactions of the use of **1** in the formation of fluorinated sulfur compounds. Although the original aim of the project proved to be more difficult to achieve than we had expected, we have discovered a novel dethioesterification reaction which afforded a possible precursor to the desired chiral stabilised carbanions. We now report the chemistry leading to the discovery of this novel reaction pathway.

The original objective of our work, which is outlined in Scheme 1, was based on the known nucleophilic attack of aliphatic thiols on **1**.[8] These results prompted us to investigate whether similar ring opening reactions would also proceed with aromatic thiols. A subsequent transformation of the expected



2 **3** **5** **4**

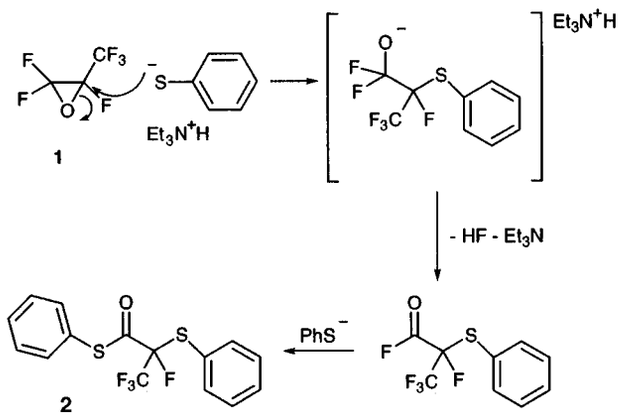
Scheme 1 Synthetic route to chiral sulfur containing compounds.

thioester **2** into the related acid **3**, followed, after resolution in the way we have previously described,[1] by oxidative decarboxylation, deprotonation and reaction with an appropriate electrophile (E^+) would then open a possible route to the synthesis of chiral sulfur compounds such as **5**.

Results and discussion

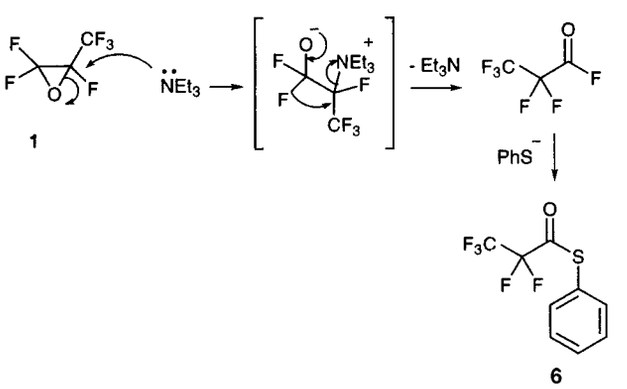
Sianesi[8] reported that the reaction of aliphatic thiols with **1** proceeded without the necessity of activation of the thiol function *e.g.* by base addition. However, in a trial reaction we found that the thiol functionality in aromatic systems shows a decreased reactivity because of its conjugation with the aromatic ring. Thus, activation, *e.g.* by the addition of a base, was required. In a first attempt triethylamine was added to thiophenol prior to reaction with **1**: two products were isolated, *S*-phenyl tetrafluoro-2-(phenylthio)propanethioate **2** (the target molecule), and the unexpected *S*-phenyl pentafluoropropanethioate **6**, in a ratio of *ca.* 1:1, this mixture could be readily separated by distillation. The structures of **6** and **2** were determined by ^{1}H, ^{19}F and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis and in the case of **6** by independent synthesis from the reaction of ethyl pentafluoropropanoate and potassium benzenethiolate. It is of interest to note that the $^3J_{FF}$ coupling follows the pattern often seen in pentafluoroethyl

groups of being zero or very small. The formation of the main product, **2**, is rationalised as shown in Scheme 2.



Scheme 2 Mechanism for the formation of *S*-phenyl tetrafluoro-2-(phenylthio)propanethioate **2**.

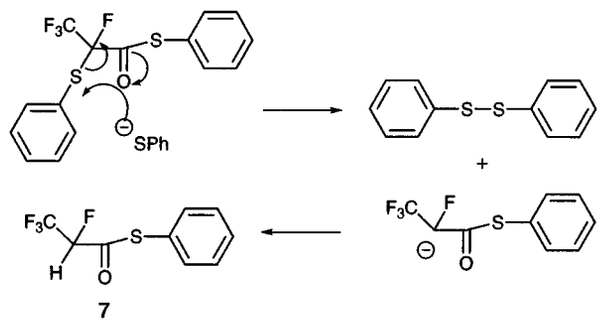
Formation of *S*-phenyl tetrafluoro-2-(phenylthio)propanethioate **2** proceeds *via* ring opening by the nucleophilic reagent to give the 1,1-difluoroalkoxide ion as an unstable intermediate. After the loss of fluoride ion, generating the acyl fluoride, a further attack of benzenethiolate on the acyl fluoride leads to the target molecule **2**. The formation of the unexpected ester *S*-phenyl pentafluoropropanethioate **6** can be explained by considering the possible role of triethylamine in the reaction. Sianesi *et al.* [8] have reported a primary amine catalyzed isomerisation of **1** to the corresponding acyl fluoride by an anionotropic rearrangement reaction. The same rearrangement could have occurred in this experiment, assuming that attack of free triethylamine gives an intermediate, which on rearrangement leads to the formation of the perfluoroacyl fluoride which can then react with thiolate ion affording the observed ester as shown in Scheme 3.



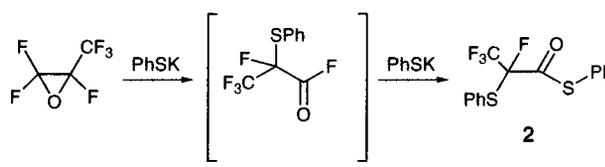
Scheme 3 Mechanism for the formation of *S*-phenyl pentafluoropropanethioate **6**.

To circumvent the anionic rearrangement reaction catalysed by tertiary amines we next studied formation of the thiolate ion using inorganic bases. The first reaction we investigated was a two-phase reaction using aqueous sodium hydroxide and ether. The reaction was carried out at room temperature using a "Drikold" condenser to contain **1**. The reaction, somewhat surprisingly, afforded *S*-phenyl tetrafluoropropanethioate **7** and diphenyl disulfide. The structure of the thioester **7** was readily confirmed by a combination of spectroscopy and elemental analysis. We rationalise this reaction as shown in Scheme 4.

There is precedent in the literature for fluorocarbanions acting as good leaving groups.[9] At this stage we cannot rule out the possibility of a radical reaction but our experience suggests the ionic process to be the more likely. It would seem that the presence of water in the system played a large part in this reaction, we therefore pre-prepared the potassium benzenethiolate by reaction of potassium hydroxide in methanol with thiophenol. After a trial experiment it was clear that it was important to ensure that the benzenethiolate was very dry, thus, it was washed several times with acetone and dried in a vacuum oven at 60 °C for 24 h. Reaction of the dried salt with **1** afforded *S*-phenyl tetrafluoro-2-(phenylthio)propanethioate **2** in 74% yield with no evidence from both NMR spectroscopy or from GC–MS for the formation of **6**, suggesting that the proposed role of triethylamine in its formation was the most likely explanation (see Scheme 5).



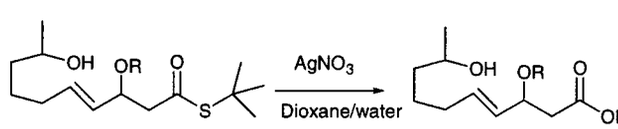
Scheme 4 Mechanism for the formation of **7**.



Scheme 5 Synthesis of **2** from **1** and potassium benzenethiolate.

The next step in the synthesis of a chiral sulfur containing compound, as illustrated in Scheme 1, was the saponification of the thioester **2** to the corresponding acid **3**. As described in the literature,[10] saponification reactions of thioesters are usually carried out in alkaline medium using excess 2 M potassium hydroxide solution. Unfortunately, in the case of *S*-phenyl tetrafluoro-2-(phenylthio)propanethioate **2**, somewhat surprisingly in view of the usual readiness with which fluoroesters hydrolyse, a mixture of unreacted thioester and target molecule tetrafluoro-2-(phenylthio)propanoic acid **3** in a ratio of approximately 2:3 in favour of **3** was obtained under the optimum reaction conditions. The acid **3** could eventually be obtained from the mixture by careful control of the pH during the work-up procedure. This involved extraction of an ethereal solution of acid **3** with saturated aqueous sodium bicarbonate, leaving most of the thiophenol reaction by-product in the ethereal layer. The structure of the acid was confirmed by a combination of the same physical methods as above.

This disappointing outcome with the incompleteness of the reaction and tedious work-up prompted us to investigate an alternative method for the hydrolysis of thioesters as reported by Gerlach *et al.*[11] as shown in the saponification of the ester to the corresponding acid in Scheme 6. Instead of potassium



Scheme 6 Gerlach's silver-mediated thioester hydrolysis.

hydroxide as the base, silver nitrate in dioxane–water was used. It is believed that the coordination of the silver atom with the sulfur activates the carbon–sulfur bond sufficiently to enhance the nucleophilic attack of the hydroxide to form the acid moiety.

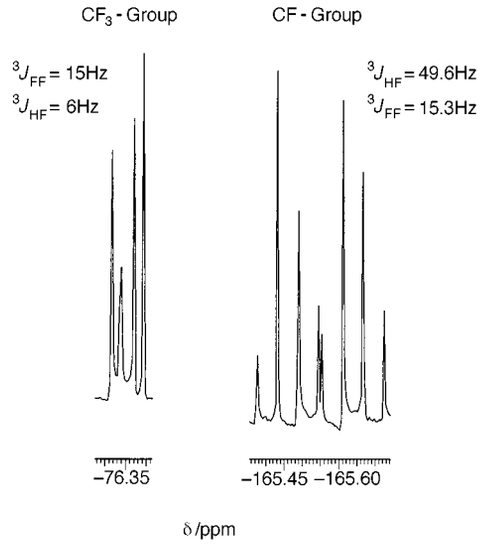


Fig. 1 ^{19}F-NMR Spectrum of 1,2,2,2-tetrafluoro-1-(phenylthio)-ethane **4**.

Using Gerlach's conditions, *S*-phenyl tetrafluoro-2-(phenylthio)propanethioate **2** and silver nitrate were heated under reflux for 4 hours in a mixture of dioxane and water (4:1). The ^{19}F-NMR spectrum of the product (instead of showing the expected doublet for the fluorine atoms of the CF_3 group at a chemical shift of about −75 ppm and the quartet for the single fluorine atom at a chemical shift of about −145 ppm) appeared more complicated. In the region of −76 ppm, the presence of a doublet of doublets indicated a further coupling of the fluorine atoms of the CF_3-group besides the 15 Hz $^3J_{FF}$ coupling to the single fluorine.

The second pattern in the ^{19}F-NMR spectrum, a doublet of quartets, underlined the existence of another coupling partner besides the coupling halogen atoms. The chemical shift of −165 ppm for the doublet of quartets gave evidence for the existence of a hydrogen atom in the new molecule. The ^{19}F-NMR spectrum recorded is shown in Fig. 1.

Considering 1,2,2,2-tetrafluoro-1-(phenylthio)ethane **4** as the product of the reaction, as shown in Scheme 7, the analytical data become understandable.

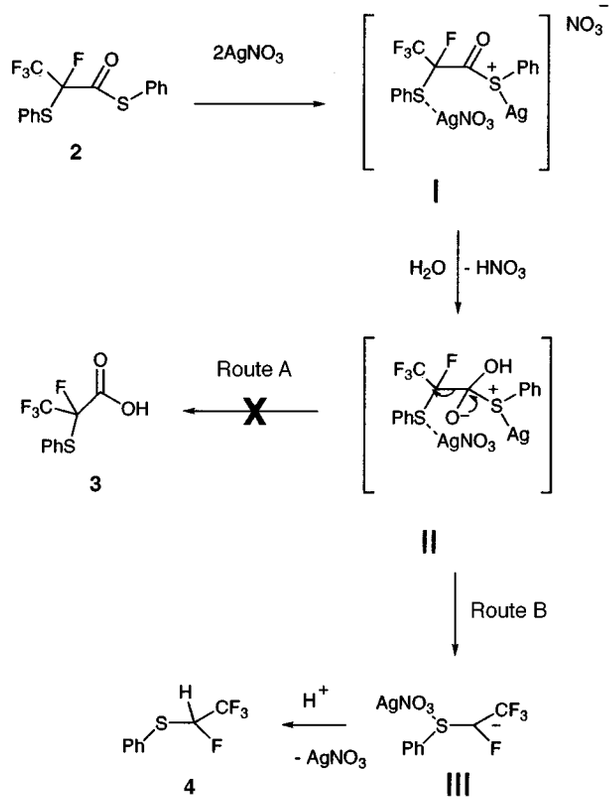
We believe that in the first step the silver atom coordinates with the readily accessible sulfur atom of the thioester functionality. The four-fold excess of silver nitrate also leads to an association between a silver atom and the second sulfur atom, as shown in intermediate **I**.

In the second step, nucleophilic attack of the hydroxide (or water) onto the carbonyl function of the thioester leads to the formation of intermediate **II** and nitric acid (visible through the evolution of NO_2).

The breakdown of alkoxide anion **II** can now occur *via* two possible reactions as shown by route A in Scheme 7. Stabilization is conceivable by the formation of 1,2,2,2-tetrafluoro-2-(thiophenyl)propanoic acid **3** and silver benzenethiolate which represents the expected reaction.

The second possibility involves the formation of carbanion **III**, as shown by route B in Scheme 7. The formation of carbanion **III** is plausible considering the stabilizing effects of its substituents: the trifluoromethyl group as an electron-withdrawing moiety, and the thiophenyl group which is positively charged due to the co-ordination with the silver atom, these effects may however be partly counterbalanced by the now well established I_π effect between the fluorine atom and the negative charge. The greater stability of carbanion **III** would explain the favourable formation of 1,2,2,2-tetrafluoro-1-(phenylthio)-ethane **4**, after protonation by the water or nitric acid present in the reaction mixture.

A third possible mechanism involves the intermediate generation of 1,2,2,2-tetrafluoro-2-(phenylthio)propanoic acid **3** and a subsequent decarboxylation reaction to form 1,2,2,2-tetrafluoro-1-(phenylthio)ethane **4**. However, we disregard this mechanism of product formation since no 1,2,2,2-tetrafluoro-2-(phenylthio)propanoic acid **3** was detectable by the analytical methods applied.



Scheme 7 Mechanism for the formation of 1,2,2,2-tetrafluoro-1-(thiophenyl)ethane **4**.

This new type of reaction, the dethioesterification reaction, provides a simple and efficient route to the synthesis of new fluorinated sulfur containing compounds possibly in a stereoselective manner *cf.* refs 1, 6 and 11. Through the new methodology the synthesis of 1,2,2,2-tetrafluoro-1-(phenylthio)ethane **4** is readily available by two methods: first the saponification reaction of the *S*-phenyl tetrafluoro-2-(phenylthio)propanethioate **2** and subsequent decarboxylation of 1,2,2,2-tetrafluoro-2-(phenylthio)propanoic acid **3**, or by the new reaction described above. The resolution of acid **3** by the method we have recently reported[1] would afford single enantiomers which on decarboxylation by the method of Rozov[5] would lead to enantiomerically pure **4**. Work is in progress to study the deprotonation reaction of **4** and quenching of the resulting anion with various electrophiles, and on decarboxylation and trapping reactions with both the racemic and resolved acids **3**.

Experimental

The ^{1}H-NMR (300 MHz) and the ^{13}C-NMR spectra (75 MHz) were measured on a Bruker AC 300 NMR spectrometer unless stated otherwise. The ^{1}H-NMR spectra (400 MHz) were measured on a Bruker AMX 400 NMR spectrometer. The ^{19}F-NMR spectra were carried out either on a JEOL NMR spectrometer, type FX 90 Q (84.26 MHz) or on a Bruker AC 300 NMR spectrometer (282.4 MHz); tetramethylsilane and fluorotrichloromethane were used as internal references. For the characterisation of the signals the following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext = sextet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, "quin" = pseudo quintet *etc.* *J* Values are given in Hz. The mass spectra (CI-MS, EI-MS) were measured

on a VG-Prospec-triple focusing mass spectrometer. For GC-MS analysis, a Carlo Erba 8000 series GC was used with a 50 meter column, BPX 5 (helium carrier gas, 70 eV, electron impact).

Thin layer chromatography was performed on TLC plastic sheets with silica gel 60 F_{254}, pre-coated with a layer thickness of 0.2 mm from Merck, Art. 5735. Gas chromatographic analysis was carried out using a Philips PYE Unicam Series 304 chromatograph with a 50 metre CD-SIL-CB 19 column. The data were registered by a JCL 600 chromatography data system. HPLC was carried out using a Gilson apparatus with a UV detector and a Techsphere 5 silica column (25 cm × 4.6 mm i.d.)

Synthesis of *S*-phenyl pentafluoropropanethioate 6 and *S*-phenyl tetrafluoro-2-(phenylthio)propanethioate 2

Hexafluoropropylene oxide **1** (10 g, 0.06 mol) was condensed over 30 min into ether (30 cm^3) in a flask equipped with a Drikold condenser, an inner thermometer and a dropping funnel cooled to −55 °C. A mixture of thiophenol (19.8 g, 0.18 mol) and triethylamine (15 g, 0.15 mol) was added dropwise (15 min) to the solution with the temperature maintained at −55 °C. After stirring for a further 30 min at −55 °C, the reaction mixture was allowed to warm to −20 °C and then allowed to react for 5 h when no more **1** was seen to reflux. The solution was then poured onto ice–water (300 cm^3) the organic layer was separated, dried (Na_2SO_4) and the solvent evaporated to leave an oil. Distillation *in vacuo* gave (i) a mixture of **6** and thiophenol, treatment of the distillate with potassium hydroxide solution (2 M), ether extraction and recovery of the product by evaporation of the ether gave *S*-phenyl pentafluoropropanethioate **6** (1.8 g), bp 48–50 °C, 0.5 mmHg, as a colourless liquid identical to a sample prepared from ethyl perfluoropropanoate and potassium benzenethiolate (Found: C, 42.02; H, 1.83%. $C_9H_5F_5OS$ requires C, 42.19; H, 1.97%): δ_H ($CDCl_3$) 7.28 (m, ArH), δ_F ($CDCl_3$) −81.7 (CF_3), −119.7 (2F, s, CF_2); δ_C ($CDCl_3$) 185.3 (t, $^2J_{CF}$ 34.8, *C*OCF), 134.1 (s, ring C, *C*S), 130.8 (s, ring C, *C-ortho*), 130 (s, ring C, *C-ortho*), 130 (s, ring C, *C-meta*), 129.5 (s, ring C, *C-para*), 117.9 (q, $^1J_{CF}$ 278.8, $^2J_{CF}$ 34.8, *C*F_3), 108.1 (tq, $^1J_{CF}$ 279, $^2J_{CF}$ 34.8, *C*F_2); *m*/*z* 256 (M^+, 24%), 228 (14), 109 (100), 77 (11), 69 (21); (ii) a residue (3.4 g) as a yellow liquid which on distillation *in vacuo* gave *S*-phenyl tetrafluoro-2-(phenylthio)propanethioate **2** (2.6 g) bp 142–146 °C/0.5 mmHg (Found: C, 51.9; H, 2.79% $C_{15}H_{10}F_4OS_2$ requires C, 52.01; H, 2.91%); δ_H ($CDCl_3$) ring (I): 7.78 (2H, d, $^3J_{HH}$ 7, 2*H*, *ortho*), 7.81 (2H, t, $^3J_{HH}$ 7, 2*H*, *meta*), 7.51 (1H, t, $^3J_{HH}$ 7, 1*H*, *para*); ring (II), 7.16 (d, $^3J_{HH}$ 7, 2H, *ortho*), 7.36 (t, $^3J_{HH}$ 7, 1H, *para*), 7.46 (t, $^3J_{HH}$ 7, 2H, *meta*); δ_F ($CDCl_3$) −74.2 (3F, d, $^3J_{FF}$ 14.5, CF_3), −143.1 (1F, q, $^3J_{FF}$ 14.5, C*F*); δ_C ($CDCl_3$) 189.3 (d, $^2J_{CF}$ 34.8, *C*OCF), 137.8 (s, ring (I) C, *C*S), 134.9 (s, ring (I) C, *C-ortho*), 131.2 (s, ring (I) C, *C-meta*), 129.9 (s, ring (I) C, *C-para*), 130.2 (s, ring (II) C, *C*S), 129 (s, ring (II) C, *C-ortho*), 127.8 (s, ring (II) C, *C-meta*), 124.2 (s, ring (II) C, *C-para*), 120.9 (qd, $^1J_{CF}$ 278.8, $^2J_{CF}$ 34.8, *C*F_3), 105 (dq, $^1J_{CF}$ 244, $^2J_{CF}$ 34.8, *C*F); *m*/*z* (EI) 346 (M^+, 40%), 218 (21), 209 (48), 137 (80), 109 (100); Found mass, 346.009753. Required mass ($C_{15}H_{10}F_4OS_2$), 346.010922.

Reaction of (1) with aqueous sodium hydroxide and thiophenol

Compound **1** (15 g) was bubbled into a vigorously stirred mixture of 2 M sodium hydroxide (100 cm^3) and ether (30 cm^3) containing thiophenol (15 g) in a flask fitted with a Drikold condenser. The reaction was continued for 4 h when no more drops of the epoxide **1** could be seen refluxing from the condenser. The yellow ether layer was separated off and combined with the ether extracts (2 × 50 cm^3) of the aqueous layer, dried ($MgSO_4$) and the ether evaporated to yield a yellow slush (4.2 g). The slush was distilled *in vacuo* to give (i) *S*-phenyl tetrafluoropropanethioate **7** (2.6 g), bp 109–110 °C/0.5 mmHg as a pale yellow oil (Found: C, 45.29; H, 2.48%. $C_9H_6F_4OS$ requires C, 45.38; H, 2.54%); δ_H ($CDCl_3$) 5.22 (1H, dq, $^2J_{HF}$ 48.8, $^3J_{HF}$ 7, CF_3CHF), 7.3–7.5 (5H, m, Ar*H*); δ_F ($CDCl_3$) −76.2 (3F, dd, $^3J_{FF}$ 14.5, $^3J_{HF}$ 7, CF_3), −202.6 (1F, dq, $^2J_{HF}$ 48.8, $^3J_{FF}$ 7, CF_3CFH); δ_C ($CDCl_3$) 184.7 (s, C=O), 137.2 (ring C, *C*S), 135 (ring C, *C-ortho*), 131 (ring C, *C-meta*), 130 (ring C, C-*para*), 120.6 (qd, $^1J_{CF}$ 279.2, $^2J_{CF}$ 34.8, CF_3), 89 (dq, $^1J_{CF}$ 209, $^2J_{CF}$ 34.8, CH*F*); *m*/*z* 238 (M^+, 36%), 210 (12), 109 (100), 101 (21), 69 (19); (ii) a residue (1.1 g) identified as diphenyl disulfide with a ^{13}C NMR spectrum and IR spectrum identical to an authentic sample.

Reaction of (1) with dry potassium benzenethiolate

Preparation of potassium benzenethiolate. Thiophenol (40 g, 37 cm^3, 0.36 mol), potassium hydroxide (20 g, 0.36 mol) and methanol (100 cm^3) were stirred together for 24 hours at room temperature. After evaporation of the solvent, the beige coloured solid was washed with acetone (2 × 100 cm^3) and dried in a vacuum oven at 60 °C for 24 h to give potassium benzenethiolate (51 g, 95%) which was used immediately.

Synthesis of *S*-phenyl tetrafluoro-2-(phenylthio)propanethioate 2. Potassium benzenethiolate (29.6 g, 0.20 mol) and tetrahydrofuran (200 cm^3) were placed in a three necked flask (equipped with a Drikold condenser, gas inlet tube and an inner thermometer) and cooled to −78 °C. Hexafluoropropylene oxide **1** (16.6 g, 0.1 mol) was added slowly over a period of 30 minutes. The cooling bath (Drikold condenser with acetone) was removed and the mixture was allowed to stir at room temperature for 15 h. The resultant bright yellow emulsion was then poured onto ice–water (300 cm^3) and the organic layer was separated. The water layer was extracted further with ether (2 × 150 cm^3). The organic layers were then combined and dried ($MgSO_4$) and the solvents evaporated to give the thioester **2** (25.6 g, 0.074 mol, 74%) as a yellow oil. Further purification was carried out by fractional distillation *in vacuo* (142–146 °C/0.5 mmHg) to give **6** (19 g) as a clear yellow oil. See Method A for analytical data.

Synthesis of 1,2,2,2-tetrafluoro-2-(phenylthio)propanoic acid 3

The ester **2** (15 g) was heated under reflux with 2 M aqueous potassium hydroxide (50 cm^3) for 18 h. The resulting suspension was cooled, extracted with ether (2 × 25 cm^3), the ether layer dried ($MgSO_4$), and the ether evaporated to yield unchanged **2** (4.2 g). The aqueous layer was acidified with conc. HCl (10 cm^3) and extracted with ether (3 × 50 cm^3). The ether layer was then extracted with saturated $NaHCO_3$ solution (2 × 50 cm^3). The residual ether solution was dried ($MgSO_4$) and evaporated to yield thiophenol (2.6 g) identical to an authentic sample. The aqueous layer was acidified and extracted with ether (3 × 25 cm^3), the ether dried ($MgSO_4$) and evaporated to leave a yellow oil (5.1 g) distillation of which *in vacuo* afforded 1,2,2,2-tetrafluoro-2-(phenylthio)propanoic acid **3** (4.6 g) bp (120–122 °C/0.5 mmHg) as an oil (Found: C, 42.31; H, 2.27; S, 12.44%. $C_9H_6F_4O_2S$ requires C, 42.52; H, 2.38; S, 12.61%); δ_H ($CDCl_3$) 10.2–10.6 (1H, br s, COO*H*), 7.35–7.65 (5H, m, Ar*H*); δ_F ($CDCl_3$) −76.3 (3F, d, $^3J_{FF}$ 14.5, CF_3), −166.2 (1F, q, $^3J_{FF}$ 14.5, C*F*CF_3); *m*/*z* 254 (M^+, 38%), 210 (48) 109 (100) 69 (23); Found mass, 254.00237. Required mass ($C_9H_6F_4O_2S$), 254.00246.

Synthesis of (*R*,*S*)-1,2,2,2-tetrafluoro-1-(phenylthio)ethane 4

S-Phenyl tetrafluoro-2-(phenylthio)propanethioate **2** (3.46 g, 0.01 mol) and silver nitrate (6.8 g, 0.04 mol) in a solvent mixture of dioxane–water 4:1 (150 cm^3) were heated under reflux for 4 h, the solution was cooled down and the silver salts were removed by filtration. On the addition of water (10 cm^3) and ether (15 cm^3), a two-phase system was obtained, from which the organic layer was separated. The water layer was extracted

further with ether (2 × 10 cm^3). The ether was distilled off with a K-piece and the remaining dioxane was removed by distillation with a column (10 cm^3 length, i.d. = 1 cm^3 packed with Fenske helices i.d. = 4 mm). The residue was distilled *in vacuo* to yield 1,2,2,2-tetrafluoro-1-(thiophenyl)ethane **7** (0.9 g, 42%), bp (40 °C/5 mmHg) (Found: C, 45.38; H, 2.64; S, 15.11%. $C_8H_6F_4S$ requires C, 45.71; H, 2.88; S, 15.26%); δ_H ($CDCl_3$) 7.62–7.54 (2H, m, ring protons 2 × C *ortho*), 7.42–7.35 (3H, m, ring protons 2 × *meta*, 1 × *para* position), 5.83 (1H, dq, $^2J_{HF} = 50$, $^3J_{HF} = 6$, C*H*F); δ_F (282.4 MHz, $CDCl_3$) −76.4 (3F, dd, $^3J_{FF} = 15$, $^3J_{HF} = 6$, CF_3), −165.6 (1F, dq, $^2J_{HF} = 49.6$, $^3J_{FF} = 15.3$, CF_3CF), δ_C ($CDCl_3$) 133.92 (ring C, *C*-ipso), 133.7 (s, ring C, 2 × *C-ortho*), 129.5 (s, ring C, 2 × *C-meta*), 129.4 (s, ring C, *C-para*), 121 (qd, $^1J_{CF} = 319$, $^2J_{CF} = 36$, CF_3), 98.6 (dq, $^1J_{CF} = 268$, $^2J_{CF} = 36.5$, *C*F), *m*/*z* 210 (M^+, 65%), 141 (35), 109 (50), 78 (90), 69 (30); Found mass, 210.012657. Required mass ($C_8H_6F_4S_1$), 210.012635.

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Paper 8/09699F