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POLYFLUOROBICYCLO(2,2,1)HEPTANES PART VII*. UNDECAFLUORO- AND 4*H*-DECAFLUORO-BICYCLO-(2,2,1)HEPTANE-1-THIOL AND RELATED BRIDGEHEAD SULPHUR COMPOUNDS

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SUMMARY

The title compounds have been prepared from 1-lithio-undecafluorobicyclo-(2,2,1)heptane and 1*H*,4-lithio-decafluorobicyclo(2,2,1)heptane, respectively, and sulphur. The undecafluorothiol was also produced from sulphur and the carbanionic intermediate generated from 1*H*-undecafluorobicyclo(2,2,1)heptane and potassium t-butoxide in dimethyl sulphoxide (DMSO). The thiols were quite acidic and were fully characterised as their disulphides, methyl thio-ethers and related compounds. A novel elimination of sulphur was observed for the undecafluorothiol under conditions which left the 4*H*-decafluoro analogue unaffected, another example of the effect of substituents at one bridgehead position on reactivities at the other.

INTRODUCTION

Perfluoroalkylthiols, prepared from the corresponding disulphides, have been described[2–5] and show a marked tendency to lose the α-fluorine atom with acceptors for hydrogen fluoride in polar solvents[5]. However, the more direct method of synthesis using sulphur and a perfluorocarbanionic species has recently been suggested by the formation of perfluoro-t-butylthiol *via* bis(perfluoro-t-butyl)mercury and sulphur in dimethyl formamide containing a catalytic amount of potassium fluoride[6].

This paper describes the syntheses of highly fluorinated bridgehead thiols from reactions of organometallics with sulphur, and illustrates further the wide synthetic utility of 1*H*-undecafluoro- and 1*H*,4*H*-decafluoro-bicyclo(2,2,1)heptane, (I) and (II), respectively.

* For Part VI, see ref. 1.

RESULTS AND DISCUSSION

The volatile and crystalline undecafluorobicyclo(2,2,1)heptan-1-ylthiol (IV) was obtained from the 1*H*-undecafluoride (I) by two routes. The first was a direct reaction involving potassium t-butoxide and sulphur in DMSO. In the second, 1-lithio-undecafluorobicyclo(2,2,1)heptane (III) was generated from (I) and butyl-lithium in ether–hexane at −78°, and was treated with sulphur. These syntheses using carbanionic intermediates, generated by removal of bridgehead hydrogen, provide another example of a general route[7,11–13] to polyfluorobicyclo(2,2,1)-heptane derivatives.

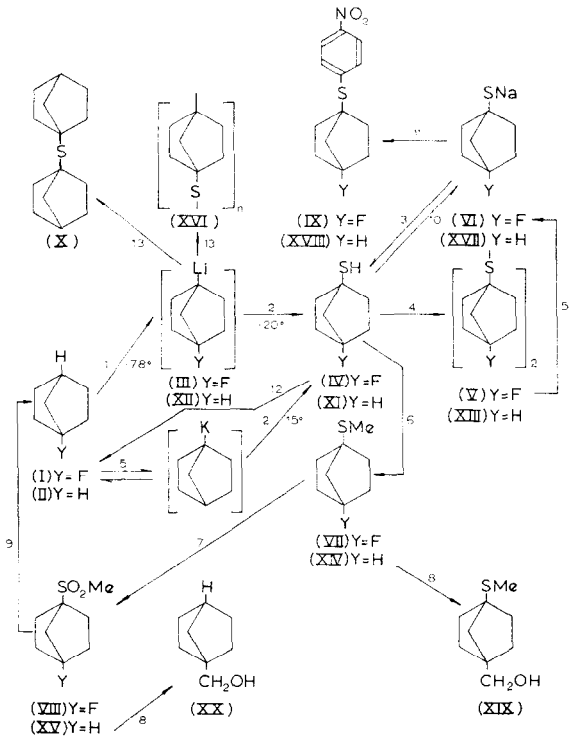

Fig. 1. Polyfluorobicyclo(2,2,1)heptane bridgehead sulphur derivatives. 1, BuLi; 2, S; 3, H_3O^+; 4, Br_2–AcOH; 5, t-BuOK–DMSO; 6, CH_3N_2; 7, H_2O_2–AcOH; 8, H_2O–KOH–DMSO–HCHO; 9, H_2O–KOH–DMSO; 10, NaOH(aq); 11, $C_6F_5NO_2$–Et_2O; 12, pyridine; 13, SCl_2.
(All unmarked substituents are fluorine.)

The total product from the potassium t-butoxide–DMSO system contained the thiol (IV), bis(undecafluorobicyclo[2,2,1]heptan-1-yl)disulphide (V) and hydrated sodium undecafluorobicyclo(2,2,1)heptane thioxide (VI). The intense colour changes observed during this reaction would be in accord with a process[8] involving attack of the polyfluorocarbanionic intermediate on the eight-membered

ring of sulphur atoms followed by successive degradation of the sulphur chain as depicted by:

$$C_7F_{11}^- + S_8 \longrightarrow C_7F_{11}S_8^- \xrightarrow{C_7F_{11}^-} C_7F_{11}S_7^- + C_7F_{11}S^-$$

Since oxygen was carefully excluded, the disulphide (V) is thought to originate from a process involving a polysulphide anion[9].

The disulphide (V) was obtained also, during the characterisation of the thiol (IV), by atmospheric oxidation in glacial acetic acid.

The thiol (IV) displayed the marked acidity to be associated with its structure, and an acceptable equivalent weight was determined by potentiometric titration in aqueous ethanol; a pK_a value of 3.2 was obtained but high accuracy is not claimed. Thiol (IV) was methylated with diazomethane to give the methyl thio-ether (VII) which was oxidised with hydrogen peroxide in acetic acid to the highly crystalline sulphone (VIII).

The disulphide (V) was reduced with zinc powder in acetic acid but gave the 1*H*-undecafluoride (I) in addition to the thiol (IV). Likewise, sodium borohydride in diglyme gave both (I) and (IV). However, in both cases the major product was the 1*H*-undecafluoride (I), and the thiol (IV) was only obtained in trace amounts. In the case of the acid reduction, the thiol (IV) was found only as a small sublimate in the condenser and not at all in the reaction mixture, indicating that it was an intermediate and had only survived by virtue of its great volatility. Such a facile loss of sulphur from the thiol (IV) (*cf.*, for example, CF_3CH_2SH[2] and $H(CF_2)_6CH_2SH$[10]) may reflect the stability of the undecafluoronorbornyl bridgehead carbanionic species functioning as a leaving group in a displacement reaction from sulphur. The disulphide (V) was cleaved to the thiol (IV) with potassium t-butoxide in DMSO.

The poor nucleophilicity anticipated for the sodium thioxide (VI) was manifested by its failure to react with decafluorocyclohexene and 2,4-dinitrochlorobenzene. However, with the highly activated pentafluoronitrobenzene at 35° it gave (4′-nitrotetrafluorophenyl)(undecafluorobicyclo[2,2,1]heptan-1-yl)sulphide (IX).

Bis(undecafluorobicyclo[2,2,1]heptan-1-yl)sulphide (X) was readily obtained from 1-lithio-undecafluorobicyclo(2,2,1)heptane[11] (III) and sulphur dichloride.

4*H*-Decafluorobicyclo(2,2,1)heptan-1-ylthiol (XI) was obtained from 1*H*,4-lithio-decafluorobicyclo(2,2,1)heptane (XII) and sulphur in ether–hexane at −78°. The same thiol was obtained in very poor yield from the 1*H*,4*H*-decafluoride (II), potassium t-butoxide and sulphur in DMSO.

The thiol (XI) was readily oxidised to the disulphide (XIII) with bromine in acetic acid and was methylated with diazomethane in ether to give the thio-ether (XIV) which was oxidised by hydrogen peroxide in acetic acid to the sulphone (XV).

It was of interest to find that the 1*H*,4-lithio compound (XII) and sulphur dichloride did not give bis(4*H*-decafluorobicyclo[2,2,1]heptan-1-yl)sulphide (*cf.* the

4*F* analogue), but a suspected poly(1-thiodecafluorobicyclo[2,2,1]hept-4-yl) (XVI) and the 1*H*,4*H*-fluorocarbon (II). The same products were obtained with the reverse mode of mixing the reagents.

As noted in earlier studies[12], equilibria are set up involving the unreacted 1*H*,4-lithio compound (XII) such as those depicted in Figure 2.

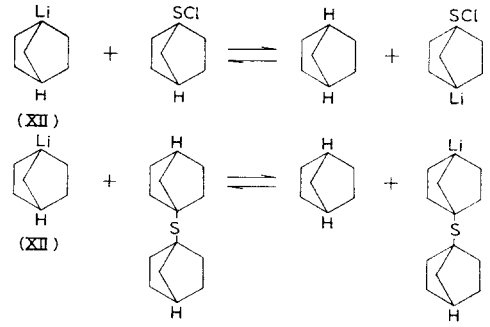

Fig. 2. Lithium exchanges with the 1*H*, 4-lithio-decafluoride (XII).
(All unmarked substituents are fluorine.)

The products of such exchanges could then enter into further reactions involving sulphur dichloride which would give rise to polymers of the type indicated.

4*H*-Decafluorobicyclo(2,2,1)heptan-1-ylthiol (XI) was acidic and titration with potassium hydroxide in aqueous ethanol gave an acceptable equivalent weight and a pK_a value of 3.3 (*cf.* a value of 3.2 for the undecafluorothiol (IV)).

Although the pK_a value of the 4*H*-decafluorothiol (XI) might be expected to be larger than that of the 4*F* analogue (IV) on the basis of a direct field-inductive effect between the bridgehead substituents (see later), the values obtained by this method are not sufficiently accurate to assess the magnitude of this interaction through the molecular cavity.

The thiol (XI) and sodium hydroxide gave the sodium thioxide (XVII), and this in turn displayed sufficient nucleophilicity to give (4′-nitrotetrafluorophenyl)-(4*H*-decafluorobicyclo[2,2,1]heptan-1-yl)sulphide (XVIII) with pentafluoronitrobenzene in diethyl ether.

The IR spectra of the four derivatives (XIII), (XIV), (XV) and (XVIII) contained the anticipated C–H stretching frequency (3030 cm^{-1} in each case) characteristic[13] of the bridgehead position of polyfluorobicyclo(2,2,1)heptanes. Hence, as in related systems, they should be convertible into carbanionic-type intermediates which are favoured stereochemically[7]. This was verified with the thio-ether (XIV) which, with formalin in aqueous DMSO containing potassium hydroxide at room temperature, gave methyl (4-hydroxymethyl-decafluorobicyclo[2,2,1]heptan-1-yl)sulphide (XIX).

However, the sulphone (XV), aqueous potassium hydroxide, DMSO and formalin gave the known[7] 1*H*,4-hydroxymethyl-decafluorobicyclo(2,2,1)heptane (XX). Presumably the favourable nature of the bridgehead carbanionic intermediate makes the polyfluoronorbornyl moiety of the sulphone a good leaving group (*cf.* $CF_2ClCFCl^-$ from $CF_2ClCFClSO_2Cl$ and the fluoride ion[14]). It is difficult to assess whether the sulphone is hydroxymethylated before or after the C–S bond cleavage. However, with aqueous potassium hydroxide and DMSO, the sulphone (XV) gave the 1*H*,4*H*-decafluoride (II). It was established also that the 4*F*-sulphone (VIII) analogously gave the 1*H*-undecafluoride (I). In view of the lability towards alkali of the S–S bond of the perfluorodisulphide (*cf.* $(CF_3S)_2$[2]), which as mentioned earlier had given the sodium thioxide (VI) with potassium t-butoxide in DMSO, the hydroxymethylation of the disulphide (XIII) was not attempted.

The cleavage of the C–S bond when the sulphones (VIII) and (XV) were treated with potassium hydroxide was not too surprising. Sulphur loss during reduction of the disulphide (V), giving the 1*H*-undecafluoride (I), was more unexpected. An even more dramatic desulphurisation was then found with the 4*F*-thiol (IV) when left in hot pyridine or lutidine. Thus, (IV) and pyridine or lutidine at 100° gave elemental sulphur and the 1*H*-undecafluoride (I). The sodium thioxide (VI) and the disulphide (V) were similarly desulphurised in pyridine at 100°.

Loss of sulphur from thiols or disulphides with such reagents does not commonly occur and this particular case may arise because of the relative stability of the bridgehead undecafluoronorbornyl carbanion in agreement with a prediction[9] that stable anions can be eliminated from thiols. It was found that the analogous 4*H*-thiol (XI) and disulphide (XIII) were much less easily desulphurised, being recovered unchanged from hot pyridine. These very significant differences in reactivity between 4*F*- and 4*H*-bridgehead substituted systems in polyfluoronorbornanes have been noted before[12,15] in a variety of situations, and there is of course a considerable difference in acidity between compounds (I) and (II). Thus, it may be that the 4*H*-decafluorobicyclo(2,2,1)heptyl carbanionic moiety is an inferior leaving group in the desulphurisation process by virtue of its lower stability. These very interesting and significant differences between fluoronorbornane derivatives with a common functional group on one bridgehead and varying substituents on the other presumably must be due, at least in part, to differing C_1–C_4 interactions within the central molecular cavity. However, we have found[12,15] that some of the differences do not correspond to classical definitions of substituent effects. It is also very pertinent that tritium exchange rates with methanolic sodium methoxide for a series of our 4-substituted-1*H*-perfluoronorbornanes do not conform to any traditional measure of substituent effects[16]. Similarly, it appears from NMR studies that long-range inductive effects are less important than through-space intramolecular electric-field effects on fluorine chemical shifts[17].

Desulphurisation of the 4*H*-disulphide (XIII) was achieved using the powerful complexing species triphenyl phosphine in dimethyl formamide to give the 1*H*,4*H*-decafluoride (II) and triphenyl phosphine sulphide. The 4*F*-thiol (IV) was also desulphurised using this reagent.

EXPERIMENTAL

Gas chromatography

Analytical work was carried out using 2 m glass columns (4 mm diam.) packed with 3% silicone gum (SE 301)–Universal B (col. A) and 10% UCON oil LB-550-X–Chromosorb P (col. B).

Mass spectra

These were measured on an A.E.I. MS9 instrument.

NMR spectroscopy

The proton and fluorine spectra were measured with a Varian HA-100 instrument at 100 MHz using tetramethylsilane as internal standard and at 94.07 MHz using trichlorofluoromethane as internal standard, respectively, except as otherwise stated.

Bis(undecafluorobicyclo[2,2,1]heptan-1-yl)disulphide (V) and undecafluorobicyclo-(2,2,1)heptan-1-ylthiol (IV)

1*H*-Undecafluorobicyclo(2,2,1)heptane (I) (10.0 g) was dissolved in a solution of potassium-t-butoxide (4.4 g) in dry DMSO (200 ml, purged with nitrogen). Sulphur (4.0 g) (dried at 110°) was added and the mixture shaken under a slight positive pressure of dry N_2 for 3.5 h, poured into a mixture of ice water (500 ml) and 4 *N* HCl (50 ml) and extracted with ether (4 × 100 ml). The combined extracts were filtered, washed (1*N* NaOH, 50 ml; water, 2 × 50 ml), dried ($MgSO_4$) and evaporated. The residue was sublimed (110°, 14 mmHg) and the pale yellow sublimate (1.9 g) recrystallised from glacial acetic acid to give bis(undecafluorobicyclo[2,2,1]heptan-1-yl) disulphide (V) (nc) (1.1 g), m.p. 96–97°, (Found: C, 26.1; S, 9.8%. $C_{14}F_{22}S_2$ requires C, 25.8; S, 9.8%), *m/e* 650 (P) ($C_{14}F_{22}S_2$), 631 ($C_{14}F_{21}S_2$), 325 ($C_7F_{11}S$); the ratio P:P+2 = 100:10.8 (*i.e.* an ion containing two sulphur atoms). The combined alkaline washings were continuously extracted with ether for 36 h, and the ether dried ($MgSO_4$), filtered, fractionally evaporated to a small volume and the residual ether removed *in vacuo*, trapped at −180° and found by IR spectroscopy to contain some thiol. The semi-solid residue was sublimed (70°, 14 mmHg) to give undecafluorobicyclo(2,2,1)heptan-1-ylthiol (IV) (nc) (1.6 g), m.p. 121–123° (sealed tube), (Found: C, 25.8; H, 0.4; F, 64.4; S, 10.2%. $C_7HF_{11}S$ requires C, 25.8; H, 0.3; F, 64.2; S, 9.8%), *m/e* 326 (P) ($C_7HF_{11}S$), 306 ($C_7F_{10}S$); the ratio P:P+2 = 100:5.5 (*i.e.* an ion containing one sulphur atom), $\nu_{max.}$ 2600 cm^{-1} (w) (SH); its ^1H NMR spectrum consisted of a singlet at 8.5 τ.

The residue (1.8 g) from the sublimation was sodium undecafluorobicyclo-(2,2,1)heptane thioxide (VI) (suspected hydrate) decomposing at 290° without melting.

Undecafluorobicyclo(2,2,1)heptan-1-ylthiol (IV) from the 1-lithio compound (III)

To a well-stirred solution of 1*H*-undecafluorobicyclo(2,2,1)heptane (I) (3.53 g) in ether (20 ml) at −78°, n-butyl-lithium in hexane (7.0 ml; 2.0 *M*) was slowly added. After 0.5 h, sulphur (2.0 g; dried at 14 mmHg over P_2O_5 for 24 h) was added and stirring continued for 2 h at −78°. The solution was allowed to attain room temperature, poured into 4 *N* HCl (50 ml), filtered and the ethereal layer separated, washed with 10% aqueous potassium hydroxide (50 ml), dried ($MgSO_4$), filtered and evaporated to dryness to yield a small amount of sulphur.

The aqueous alkaline extract was acidified with HCl and ether-extracted (1 × 50 ml and 1 × 15 ml), the extracts dried ($MgSO_4$), filtered and evaporated and the residue sublimed (70°, 14 mmHg) to give undecafluorobicyclo(2,2,1)heptan-1-ylthiol (IV) (0.82 g), m.p. 119–121°, with a correct IR spectrum.

Oxidation of undecafluorobicyclo(2,2,1)heptan-1-ylthiol (IV)

Sodium undecafluorobicyclo(2,2,1)heptane thioxide hydrate (VI) (0.3 g) in glacial acetic acid (5 ml) at *ca.* 100° for 10 h gave, when cooled, bis(undecafluorobicyclo[2,2,1]heptan-1-yl) disulphide (V) (0.07 g) with a correct IR spectrum.

Acidity of the undecafluorothiol (IV)

The thiol (IV) (9.4 mg) was dissolved in ethanol (10 ml, purged with N_2), degassed water (10 ml) added and the solution titrated with 0.494 *N* NaOH from a microburette using a Pye potentiometer and a glass/calomel electrode system (previously calibrated with buffer solution) until the pH change on further addition of base was negligible. The titration was carried out as rapidly as accuracy would allow, and the cell kept covered to minimise evaporation and atmospheric oxidation. A plot of pH against the volume of base added gave an equivalent weight of 318, a duplicate on the thiol (IV) (8.9 mg) giving 327 ($C_7HF_{11}S$ requires 326). (A plot of pH against $\log_{10}[b/(a-b)]$, where a = number of moles of thiol and b = number of moles of base, was a curve with an intercept at pH 3.2.)

Methyl undecafluorobicyclo(2,2,1)heptane sulphide (VII) and the sulphone (VIII)

Sodium undecafluorobicyclo(2,2,1)heptane thioxide hydrate (VI) (2.3 g) and 4 *N* HCl (20 ml) were shaken together for 5 min, and the mixture extracted with ether (3 × 10 ml). The extracts were dried ($MgSO_4$), filtered and added dropwise to freshly prepared ethereal diazomethane at 0°, and (after 5 min) the mixture was allowed to warm slowly to room temperature. After standing for 5 h, the mixture was distilled until the distillate became colourless (diazomethane then destroyed with benzoic acid). The residual liquid was fractionally distilled to give ether and

a mixture which was separated by GLC (col. A; 120°) to give ether and a pale yellow solid which was sublimed (from P_2O_5) (100°, 14 mmHg) to give methyl undecafluorobicyclo(2,2,1)heptane sulphide (VII) (nc) (1.2 g), m.p. 61–62°, (Found: C, 28.1; H, 0.9; S, 9.9%. $C_8H_3F_{11}S$ requires C, 28.2; H, 0.9; S, 9.4%), *m/e* 340 ($C_8H_3F_{11}S$), 325 ($C_7F_{11}S$), 321 ($C_8H_3F_{10}S$); its ^1H NMR spectrum consisted of a singlet at 7.6 τ.

The sulphide (VII), obtained as above from the thiol (IV) (0.6 g), was refluxed in glacial acetic acid (10 ml), 90% H_2O_2 (3 ml) and water (3 ml) for 2 h, and the solution cooled, filtered and poured into water. The crystalline precipitate was washed with water, dried *in vacuo* (P_2O_5) and sublimed (120°, 14 mmHg) to give methyl undecafluorobicyclo(2,2,1)heptane sulphone (VIII) (nc) (0.4 g), m.p. 106°, (Found: C, 25.9; H, 0.8; S, 8.7%. $C_8H_3F_{11}O_2S$ requires: C, 25.8; H, 0.8; S, 8.6%), *m/e* 372 (vw) ($C_8H_3F_{11}O_2S$), 357 ($C_7F_{11}O_2S$), 353 ($C_8H_3F_{10}O_2S$), $\nu_{max.}$ 1329 and 1159 cm^{-1} (>SO_2); its ^1H NMR spectrum consisted of a singlet at 6.8 τ.

Reduction of bis(undecafluorobicyclo[2,2,1]heptan-1-yl)disulphide (V)

This compound (1.0 g) in glacial acetic acid (25 ml) was stirred at 80° and zinc powder (2.5 g) added, the temperature raised to 100° and stirring continued for 4.5 h; during this time a moist lead acetate paper in the condenser blackened. A small, waxy sublimate was removed from the condenser and shown (IR) to be a mixture of 1*H*-undecafluorobicyclo(2,2,1)heptane (I) and undecafluorobicyclo-(2,2,1)heptan-1-ylthiol (IV). The solution was extracted with ether (4 × 25 ml), the extracts evaporated, the residual ether removed *in vacuo*, trapped at −180° and shown by IR spectroscopy to contain 1*H*-undecafluorobicyclo(2,2,1)heptane (I).

A solution of $NaBH_4$ (0.1 g) in diglyme (5 ml, $NaBH_4$ dried) was added dropwise over 10 min to a stirred suspension of the disulphide (V) (0.65 g) in dry diglyme (10 ml). After 1 h, 4*N* HCl (5 ml) was added and a moist lead acetate paper at the mouth of the drying tube was blackened. Water (100 ml) was added, and the mixture extracted with ether (4 × 25 ml), the extracts evaporated, the residual ether removed *in vacuo*, trapped at −180° and shown by IR spectroscopy to contain both 1*H*-undecafluorobicyclo(2,2,1)heptane (I) and undecafluorobicyclo(2,2,1)-heptan-1-ylthiol (IV). The residue was shown to contain the thiol by IR spectroscopy and mass spectrometry.

Cleavage of bis(undecafluorobicyclo[2,2,1]heptan-1-yl)disulphide (V)

The disulphide (V) (0.5 g) was added to potassium t-butoxide (0.5 g) in dry DMSO (25 ml) and the solution shaken under nitrogen for 4.5 h and then poured into a mixture of ice water (100 ml) and 4 *N* HCl (10 ml) and extracted with ether (4 × 25 ml). The extracts were washed (1 *N* NaOH, 10 ml; water, 2 × 10 ml), dried and evaporated to a trace amount of tar. The combined alkaline and aqueous washings were continuously extracted with ether for 36 h, and the ether dried ($MgSO_4$), filtered and fractionated to a small volume. The remaining ether was

evaporated *in vacuo*, trapped at −180° and shown by IR spectroscopy to contain undecafluorobicyclo(2,2,1)heptan-1-ylthiol (IV). The residue (0.43 g) was hydrated sodium undecafluorobicyclo(2,2,1)heptane thioxide (VI) with a correct IR spectrum.

(4'-Nitrotetrafluorophenyl)(undecafluorobicyclo[2,2,1]heptan-1-yl)sulphide (IX)

The hydrated thioxide (VI) made *via* potassium t-butoxide (0.5 g) and pentafluoronitrobenzene (0.29 g) in ether (5 ml) was refluxed for 3.5 h and the mixture cooled, filtered and distilled *in vacuo*. The solid residue was recrystallised from ethanol, sublimed (110°, 0.01 mmHg) and recrystallised again from ethanol to give (4'-nitrotetrafluorophenyl)(undecafluorobicyclo[2,2,1]heptan-1-yl)sulphide (IX) (nc) (0.13 g), m.p. 77–79°, (Found: C, 30.3; N, 2.7; S, 6.1%. $C_{13}F_{15}NO_2S$ requires C, 30.1; N, 2.7; S, 6.2%), *m/e* 519 ($C_{13}F_{15}NO_2S$), 500 ($C_{13}F_{14}NO_2S$), 325 ($C_7F_{11}S$), 226 ($C_6F_4NO_2S$), $\nu_{max.}$ 1623 cm^{-1} (fluorinated aromatic ring); its ^{19}F NMR spectrum indicated the presence of an undecafluoronorborn-1-yl group and in addition contained two singlets at 113.8 and 116.5 (aromatic fluorines).

Bis(undecafluorobicyclo[2,2,1]heptan-1-yl)sulphide (X)

To 1*H*-undecafluorobicyclo(2,2,1)heptane (3.0 g) in ether (20 ml) at −78°, 2.0 *M* n-butyl-lithium in hexane (5.0 ml) was slowly added. The mixture was stirred for 0.5 h and a solution of sulphur dichloride (0.58 g) in ether (5.0 ml) was slowly added. The colour of the sulphur dichloride was rapidly discharged and a precipitate formed. Stirring was maintained for 1 h while the reaction mixture was allowed to attain room temperature. The reaction mixture was filtered through silica gel and evaporated to leave a solid residue (~1 g) which was sublimed (100–120°, 14 mmHg) to yield a white crystalline sublimate (0.78 g), m.p. 106–108°, and a small amount of involatile tar. A portion of the sublimate was recrystallised from ethanol to give bis(undecafluorobicyclo[2,2,1]heptan-1-yl)sulphide (X) (nc) (0.30 g), m.p. 131–132°, (Found: C, 27.1; F, 67.3; S, 4.9%. $C_{14}F_{22}S$ requires C, 27.2; F, 67.6; S, 5.2%).

4H-Decafluorobicyclo(2,2,1)heptan-1-ylthiol (XI)

To a well-stirred solution of 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (II) (10.0 g) in ether (60 ml) at −78°, 2.3 *M* n-butyl-lithium in hexane (15 ml) was slowly added. After 0.5 h, sulphur (6.0 g), dried (P_2O_5) at 0.01 mmHg for 24 h, was added, the solution kept for 0.5 h at −78°, warmed to room temperature during 1 h and poured into 4 *N* HCl (100 ml), filtered and the ethereal layer separated. It was washed with aqueous KOH, water, dried ($MgSO_4$), filtered, evaporated and the residue sublimed (40°, 14 mmHg) to give the 1*H*,4*H*-decafluoride (II) (0.60 g) with a correct IR spectrum.

The aqueous alkaline washing was acidified with 4 *N* HCl and extracted with ether, the extracts affording a residue which was sublimed (60°, 14 mmHg)

to yield 4*H*-decafluorobicyclo(2,2,1)heptan-1-ylthiol (XI) (nc) (3.56 g), m.p. 117–119°, (Found: C, 26.9; H, 0.8; F, 61.9; S, 10.6%. $C_7H_2F_{10}S$ requires C, 27.3; H, 0.6; F, 61.7; S, 10.4%), $\nu_{max.}$ 2600 cm^{-1} (w) (SH); its ^1H NMR spectrum (Perkin–Elmer R14) (in CCl_4) consisted of a sharp singlet at 7.8 τ and a broad singlet at 6.5 τ with respect to tetramethylsilane as an external reference in the relative intensity ratio of 1:1; the ^{19}F NMR spectrum (Perkin–Elmer R10) (in CCl_4) was consistent with the presence of the decafluoronorbornane unit.

Reaction of 1H,4H-decafluorobicyclo(2,2,1)heptane (II) with sulphur and potassium t-butoxide in DMSO

Compound (II) (5.6 g), anhydrous DMSO (100 ml), dry (P_2O_5) sulphur (2.0 g) and potassium t-butoxide (2.2 g) were shaken together under nitrogen for 3.5 h. The solution was poured into 10% (v/v) HCl (550 ml) and extracted with ether (2 × 100 ml). The ether extract was washed with 10% w/v aqueous KOH, dried ($MgSO_4$) and evaporated to dryness. Sublimation (90°, 14 mmHg) yielded 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (II) (0.36 g) with a correct IR spectrum.

The alkaline extract was acidified and extracted with ether (2 × 50 ml). The dried ($MgSO_4$) extract was filtered, evaporated to dryness and sublimed (90°, 14 mmHg) to give 4*H*-decafluorobicyclo(2,2,1)heptan-1-ylthiol (XI) (0.05 g) with a correct IR spectrum.

Acidity of the 4H-decafluorothiol (XI)

The thiol (XI) (41.7 mg) was dissolved in ethanol (5 ml), degassed water (5 ml) added and the solution titrated with 0.0405 *N* KOH as described for thiol (IV). A plot of pH against volume of base added gave an equivalent of 313 ($C_7H_2F_{10}S$ requires 308). (A plot of pH against $\log_{10}[b/(a-b)]$, where a = number of moles of thiol and b = number of moles of base, was a curve with an intercept at 3.3.)

Bis(4H-decafluorobicyclo[2,2,1]heptan-1-yl)disulphide (XIII)

4*H*-Decafluorobicyclo(2,2,1)heptan-1-ylthiol (XI) (0.53 g) and bromine (0.5 ml) in glacial acetic acid (4.0 ml) were stirred together for 1 h at room temperature and then poured into water (30 ml). Excess bromine was destroyed with sodium metabisulphite and after extraction with ether (1 × 10 ml + 2 × 5 ml) the extracts were washed with saturated sodium hydrogen carbonate solution until effervescence ceased, dried ($MgSO_4$) and evaporated. The residue was sublimed (140°, 14 mmHg) to yield bis(4*H*-decafluorobicyclo[2,2,1]heptan-1-yl)disulphide (XIII) (nc) (0.25 g), m.p. 110–112°, (Found: C, 27.3; F, 61.8; S, 10.3%. $C_{14}H_2F_{20}S_2$ requires C, 27.4; F, 61.8; S, 10.4%); $\nu_{max.}$ 3030 cm^{-1} (w) (bridgehead CH), *m/e* 614 (P); the ratio P:P + 2 = 100:9 (*i.e.* an ion containing two sulphur atoms).

Methyl 4H-decafluorobicyclo(2,2,1)heptane sulphide (XIV) and the sulphone (XV)

Diazomethane was distilled into 4*H*-decafluorobicyclo(2,2,1)heptan-1-ylthiol (XI) (1.93 g) in ether (30 ml) until the solution became yellow. After 15 h, excess

diazomethane was destroyed with acetic acid in ether and the solution was then washed with saturated sodium hydrogen carbonate. The ether layer was dried ($MgSO_4$), filtered, evaporated and the residue sublimed (90°, 14 mmHg) to yield a waxy material (1.2 g) which was resublimed from phosphoric oxide (90°, 14 mmHg) to yield methyl 4*H*-decafluorobicyclo(2,2,1)heptane sulphide (XIV) (nc) (0.98 g), m.p. 46–49° (sealed tube), (Found: C, 29.9; H, 1.5; F, 59.1; S, 9.7%. $C_8H_4F_{10}S$ requires C, 29.8; H, 1.2; F, 59.0; S, 9.9%), *m/e* 322 (P), $\nu_{max.}$ 3030 cm^{-1} (bridgehead CH); its ^1H NMR spectrum (Perkin–Elmer R14) (in CCl_4) consisted of a broad singlet at 6.5 τ and a sharp singlet at 7.5 τ with respect to tetramethylsilane as external reference in the relative intensity ratio of 1:3, respectively; the ^{19}F NMR spectrum (Perkin–Elmer R10) (in CCl_4) was consistent with the presence of the decafluoronorbornyl unit.

The thio-ether (XIV) (0.58 g), acetic acid (10 ml), water (3 ml) and 90% w/w hydrogen peroxide (3 ml) were refluxed together for 2 h. The cooled solution was poured into water (200 ml) and a portion (0.44 g) of the dried crystalline precipitate (0.5 g) was recrystallised from aqueous ethanol to give methyl 4*H*-decafluorobicyclo(2,2,1)heptane sulphone (XV) (nc) (0.41 g), m.p. 133–134°, (Found: C, 27.1; H, 1.3; F, 54.1; S, 9.3%. $C_8H_4F_{10}O_2S$ requires C, 27.1; H, 1.1; F, 53.7; S, 9.0%), $\nu_{max.}$ 3030 cm^{-1} (bridgehead CH), *m/e* 275 (C_7HF_{10}), 79 (CH_3O_2S) (no molecular ion was produced).

*(4′-Nitrotetrafluorophenyl)(4*H*-decafluorobicyclo[2,2,1]heptan-1-yl)sulphide (XVIII)*

A mixture of 4*H*-decafluorobicyclo(2,2,1)heptan-1-ylthiol (XI) (1.0 g), water (40 ml) and sodium hydroxide (3.0 g) was continuously extracted with ether for 3 days. The ether extract was dried ($MgSO_4$), filtered and evaporated to leave the sodium salt of the thiol (XVII) (0.26 g); this was dissolved in ether (10 ml) and pentafluoronitrobenzene (0.18 g) added. The mixture was stirred for 3 days, filtered and evaporated to an oil (0.13 g) which slowly solidified and was recrystallised from hexane to give (4′-nitrotetrafluorophenyl)(4*H*-decafluorobicyclo[2,2,1]heptan-1-yl)-sulphide (XVIII) (nc) (0.07 g), m.p. 79–81°, $\nu_{max.}$ 3030 cm^{-1} (w) (bridgehead CH), 1625 cm^{-1} (m) (fluorinated aromatic ring), *m/e* 500.947945 (P) ($C_{13}HF_{14}NO_2S$ requires 500.950427, allowed tolerance ±0.005), 482 (P—F), 226 ($C_6F_4NO_2S$); its ^{19}F NMR spectrum (Perkin–Elmer R10) (in ether) contained two singlets of equal intensity at about 149 ppm with respect to CCl_3F as internal reference (fluorines at C_2, C_3, C_5 and C_6 in benzene ring) in addition to bands characteristic of the decafluoronorbornyl unit.

*Reaction of 1*H*,4-lithio-decafluorobicyclo(2,2,1)heptane with sulphur dichloride*

To 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (II) (3.2 g) in ether (20 ml) at −78°, 2.0 *M* n-butyl-lithium in hexane (6.0 ml) was added and the mixture stirred for 0.5 h. A solution of sulphur dichloride (0.5 g) in ether (3 ml) was then added;

this mixture was stirred for 0.5 h, allowed to attain room temperature, filtered and the residue Soxhlet-extracted with ether for 15 h. The combined filtrate and extract were evaporated to low bulk and shown by GLC (DIDP–Chromosorb P, 1:10; 120°; N_2, 3 l h^{-1}) to contain 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (II). The ethereal layer was evaporated to dryness and starting material removed *in vacuo* to leave a polymeric material (1.0 g) which was Soxhlet-extracted with water for 15 h and dried (P_2O_5) *in vacuo* (100°; 14 mmHg) for 15 h to yield a suspected poly(1-thiodecafluorobicyclo[2,2,1]hept-4-yl) (XVI) (1.0 g), m.p. > 360°, (Found: C, 28.3; F, 58.7; S, 8.2%. $C_7F_{10}S$ requires C, 27.4; F, 62.1; S, 10.5%).

With reverse addition

To 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (II) (3.80 g) in ether (25 ml) at −78° was added a 2 *M* solution of n-butyl-lithium in hexane (7.0 ml). After stirring for 0.5 h, the latter solution was slowly added to sulphur dichloride (0.55 g) in ether (10 ml) at −78°, the mixture stirred for 0.5 h and allowed to attain room temperature. As before, the combined filtrate and extract were evaporated to low bulk and shown by GLC (col. B; 85°; N_2, 3 l h^{-1}) to contain the 1*H*,4*H*-decafluoride (II) (*ca.* 1.0 g by comparison with a standard solution). Evaporation of the solution gave a tarry residue (1.88 g). The residue from the extraction was Soxhlet-extracted with water for 15 h and dried (P_2O_5) *in vacuo* (100°) for 15 h to yield the suspected poly(1-thiodecafluorobicyclo[2,2,1]hept-4-yl) (XVI) (0.34 g) with a correct IR spectrum.

*Hydroxymethylation of methyl 4*H*-decafluorobicyclo(2,2,1)heptane sulphide (XIV)*

Sulphide (XIV) (1.90 g), water (1 ml), DMSO (5 ml) and KOH (0.4 g) were stirred until homogeneous when 40% formalin (0.5 ml) was added. The mixture was stirred for 24 h, poured into water (25 ml) and extracted with ether (3 × 10 ml). The combined extracts were dried ($MgSO_4$), filtered and evaporated to leave a residue which was sublimed (90°, 14 mmHg) to give methyl (4-hydroxymethyl-decafluorobicyclo[2,2,1]heptan-1-yl)sulphide (XIX) (nc) (0.54 g), m.p. 75–77°, $\nu_{max.}$ 3330 cm^{-1} (s) (OH), *m/e* 351.998146 (P) ($C_9H_6F_{10}OS$ requires 351.997956, allowed tolerance ±0.005). Its ^1H NMR spectrum (Perkin–Elmer R10) (in CCl_4) consisted of a singlet at 7.55 τ (CH_3), a singlet at 5.55 τ (CH_2) and a singlet at 5.8 τ (OH), with respect to tetramethylsilane as external reference, in the relative intensity ratio 3:2:1. Its ^{19}F NMR spectrum (Perkin–Elmer R10) (in CCl_4) was consistent with the presence of the decafluoronorbornane unit.

*Attempted hydroxymethylation of methyl 4*H*-decafluorobicyclo(2,2,1)heptane sulphone (XV)*

Sulphone (XV) (0.2 g), water (1 ml), DMSO (5 ml) and KOH (0.04 g) were stirred until all the KOH had dissolved. Formalin (0.1 ml; 40% w/v) was then added, the mixture stirred for 72 h and poured into water (50 ml). The aqueous solution was acidified with 4 *N* HCl (20 ml), extracted with ether (1 × 30 ml

+ 2 × 20 ml) and the combined extracts dried ($MgSO_4$), filtered and evaporated to leave a sticky residue which was crystallised from hexane to give 1*H*,4-hydroxymethyl-decafluorobicyclo(2,2,1)heptane (XX) (0.02 g), m.p. 160–163° (lit.[7] 176.5–177.5°) with a correct IR spectrum, *m/e* 306 ($C_8H_4F_{10}O^+$).

Base-catalysed hydrolysis of methyl 4H-decafluorobicyclo(2,2,1)heptane sulphone (XV)

Sulphone (XV) (0.04 g), water (0.5 ml), DMSO (2.0 ml) and potassium hydroxide (0.07 g) were stirred together for 68 h at room temperature. Water (4.0 ml), ether (2.0 ml) and conc. HCl (0.5 ml) were then added and the mixture stirred for 2 h. The ether layer was shown by GLC (col. B; 80°; N_2, 3 l h^{-1}) to contain 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (II). The total reaction mixture was extracted with ether and the extracts dried ($MgSO_4$), filtered and evaporated, but sulphone (XV) was not detected.

Base-catalysed hydrolysis of methyl undecafluorobicyclo(2,2,1)heptane sulphone (VIII)

Sulphone (VIII) (0.30 g), water (4 ml), DMSO (15 ml) and potassium hydroxide (0.40 g) were stirred together for 40 h, poured into 50% HCl (100 ml) and extracted with ether. The ether extract was dried ($MgSO_4$), filtered and evaporated and shown by GLC (col. B; 80°; N_2, 3 l h^{-1}) to contain 1*H*-undecafluorobicyclo-(2,2,1)heptane (I). When the latter solution was evaporated to dryness, it gave unchanged sulphone (VIII) (0.07 g) with a correct IR spectrum.

Desulphurisation of undecafluorobicyclo(2,2,1)heptan-1-ylthiol (IV)

(a) In pyridine

Thiol (IV) (0.64 g) and pyridine (4 ml) at 100° gave a dark solution and a solid was precipitated progressively. After 5.5 h at 100°, this was filtered off and shown to be sulphur (0.04 g, m.p. 119°). The cold solution was poured into 50% HCl (60 ml) and extracted with ether (3 × 10 ml). The combined extracts were dried ($MgSO_4$), filtered, evaporated to small volume and filtered. The filtrate was shown by GLC (col. B; 80°; N_2, 3 l h^{-1}) (comparison with a standard solution of the undecafluoride in ether) to contain 1*H*-undecafluorobicyclo(2,2,1)heptane (I) (0.24 g).

(b) In lutidine

Thiol (IV) (0.55 g) and lutidine (6.5 ml) were kept at 100° for 3 h and, as described previously, gave 1*H*-undecafluorobicyclo(2,2,1)heptane (I) as the sole product, as shown by GLC analysis (col. B; 80°; N_2, 3 l h^{-1}) of the ethereal extract.

(c) In dimethyl formamide–triphenyl phosphine

Thiol (IV) (0.72 g), triphenyl phosphine (0.50 g) and dimethyl formamide (3.0 ml) were kept at 100° for 3 h. The cold solution was poured into 4 *N* HCl

(20 ml) and extracted with ether. The dried ($MgSO_4$) extract was shown by GLC (col. B; 80°; N_2, 3 l h^{-1}) to contain 1*H*-undecafluorobicyclo(2,2,1)heptane (I) but none of the thiol (IV). Evaporation of the ether solution gave triphenyl phosphine sulphide (0.08 g), m.p. 159–161°, [*m/e*, 294 (P) ($C_{18}H_{15}PS^+$), 262 ($C_{18}H_{15}P^+$) and 185 ($C_{12}H_{10}P^+$)]; a sticky residue (0.16 g) was shown by mass spectrometry to be impure triphenyl phosphine sulphide.

Desulphurisation of sodium undecafluorobicyclo(2,2,1)heptane thioxide hydrate (VI)

This compound (0.3 g) in pyridine (5 ml) was heated to 100° when the solution darkened and a precipitate of sulphur quickly formed. After 3 h, the mixture was cooled and poured into 4 *N* HCl (20 ml) at 0° when H_2S was detected (smell and moist lead acetate paper). The mixture was extracted with ether (4 × 10 ml) and the extracts washed (1 *N* NaOH, 3 ml; water, 2 × 5 ml), dried ($MgSO_4$), filtered and fractionated to a small volume. The residual ether was removed *in vacuo*, trapped at −180° and shown (IR) to contain only 1*H*-undecafluorobicyclo(2,2,1)-heptane (I) (0.15 g). The combined alkaline and water washings were continuously extracted with ether for 24 h. The usual isolation procedure showed it to be devoid of fluorocarbon.

Desulphurisation of bis(undecafluorobicyclo[2,2,1]heptan-1-yl)disulphide (V)

Disulphide (V) (0.17 g) and pyridine (5.5 ml) were kept at 100° for 3 h, then cooled, poured into conc. HCl (100 ml) and extracted with ether. The dried ($MgSO_4$) ether solution was shown by GLC (col. B; 80°; N_2, 3 l h^{-1}) to contain ether, 1*H*-undecafluorobicyclo(2,2,1)heptane (I) and starting material; when evaporated to dryness it gave the disulphide (V) (0.04 g) with a correct IR spectrum and a small amount of sulphur.

Attempted desulphurisation of 4H-decafluorobicyclo(2,2,1)heptan-1-ylthiol (XI)

Thiol (XI) (0.19 g) and pyridine (3 ml) were kept at 100° for 3 h, but no precipitate formed. The solution was cooled, poured into 4 *N* HCl (20 ml) and extracted with ether (5 ml). The ethereal layer was dried ($MgSO_4$), filtered and evaporated to give the thiol (0.15 g) (XI) with a correct IR spectrum.

Attempted desulphurisation of bis(4H-decafluorobicyclo[2,2,1]heptan-1-yl)disulphide (XIII)

Disulphide (XIII) (0.26 g) and pyridine (4.0 ml) were kept at 100° for 3 h (no precipitate) and the cooled solution poured into conc. HCl (20 ml) and extracted with ether (1 × 10 ml + 2 × 5 ml). The extracts were dried ($MgSO_4$), filtered, evaporated to a small volume and shown by GLC (col. B; 80°; N_2, 3 l h^{-1}) to contain ether and starting material only. The latter solution was evaporated and the residue sublimed (100°, 14 mmHg) to give the disulphide (XIII) (0.18 g) with a correct IR spectrum.

Desulphurisation of bis (4H-decafluorobicyclo[2,2,1]heptan-1-yl)disulphide (XIII) with triphenyl phosphine

Disulphide (XIII) (0.18 g), triphenyl phosphine (0.2 g) and dimethyl formamide (3.0 ml) were kept at 100° for 3 h, cooled, poured into 4 *N* HCl (20 ml) and extracted with ether. The extract was dried ($MgSO_4$), shown by GLC (col. B; 80°; N_2, 3 l h^{-1}) to contain 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (II), and evaporated to a solid (0.17 g) shown by mass spectrometry to be impure triphenyl phosphine sulphide, and by TLC to be devoid of unchanged disulphide (XIII).

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