Partially Fluorinated Heterocyclic Compounds. Part 14.[1] Syntheses of 4,5,6,7-Tetrafluoro-2,3-dihydro-2-methyl-1-benzothiophen and 5,6,7,8-Tetrafluorothiochroman from Pentafluorophenyl Prop-2-enyl Sulphide *via* the Claisen Rearrangement Intermediate and the Related Reaction of Prop-2-enyl 2,3,5,6-Tetrafluorophenyl Sulphide. Reactions which appear to proceed *via* Homolytic Fission of an Aliphatic Carbon–Fluorine Bond

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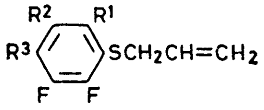
Prop-2-enyl 2,3,4,5-tetrafluorophenyl sulphide (1) undergoes a Claisen rearrangement in *NN*-diethylaniline to give 4,5,6,7-tetrafluoro-2,3-dihydro-2-methyl-1-benzothiophen (4) and 5,6,7,8-tetrafluorothiochroman (5). Pentafluorophenyl prop-2-enyl sulphide (3) in *NN*-diethylaniline also gave (4) and (5) accompanied by prop-2-enyl 3,4,5,6-tetrafluoro-2-(prop-2-enyl)phenyl sulphide (10), ethyl pentafluorophenyl sulphide (9), and perfluoropoly(phenylene sulphide). Prop-2-enyl 2,3,5,6-tetrafluorophenyl sulphide (2) reacted similarly to give 4,6,7-trifluoro-2,3-dihydro-2-methyl-1-benzothiophen (6), 5,7,8-trifluorothiochroman (7), ethyl 2,3,5,6-tetrafluorophenyl sulphide (8), and *N*-ethylaniline. Homolytic fission of the aliphatic C–F bond in the respective Claisen rearrangement intermediates from (3) and (2) is proposed to account for the formation of (4), (5), and (10), and of (6) and (7). Compounds (8)—(10) were synthesised by other methods.

THERMALLY induced reactions of pentafluorophenyl prop-2-enyl ether,[2] prop-2-enyl 2,3,5,6-tetrafluoro-4-pyridyl ether,[3] and prop-2-enyl 2,4,5,6-tetrafluoro-3-pyridyl ether [3] have been shown to give a variety of products all of which arise from the corresponding 2,4-dienone intermediate {formed *via* an initial [3,3] sigmatropic shift (the Claisen rearrangement)} which, having no *ortho*-hydrogens, is not able to enolise to the phenolic compound. Only in the case of 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-enyl ether has the initial rearrangement intermediate been isolated,[4] although 2,3,4,5,6-pentafluoro-4-(prop-2-enyl)cyclohexa-2,5-dienone was obtained by the vapour-phase pyrolysis of pentafluorophenyl prop-2-enyl ether at 365 °C, the result of a Cope rearrangement on the intermediate 2,3,4,5,6-pentafluoro-6-(prop-2-enyl)cyclohexa-2,4-dienone.[5]

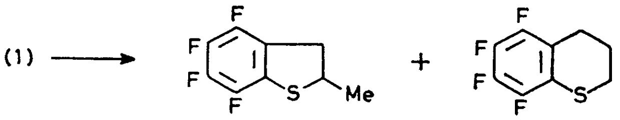


(1) $R^1 = H, R^2 = R^3 = F$
(2) $R^1 = R^2 = F, R^3 = H$
(3) $R^1 = R^2 = R^3 = F$

In this paper we report an investigation of the thermally induced reactions of some polyfluoroaryl prop-2-enyl *sulphides:* the 2,3,4,5- and 2,3,5,6-tetrafluoro-, and pentafluoro-phenyl compounds (1), (2), and (3), which were readily prepared from 2,3,4,5-tetrafluorothiophenol,[6] 2,3,5,6-tetrafluorothiophenol,[7] and pentafluorothiophenol,[7] respectively, by treatment with n-butyl-lithium and prop-2-enyl bromide.

Prop-2-enyl 2,3,4,5-tetrafluorophenyl sulphide (1), heated in refluxing *NN*-diethylaniline for 23 h, gave 4,5,6,7-tetrafluoro-2,3-dihydro-2-methyl-1-benzothiophen (4) (30%) and 5,6,7,8-tetrafluorothiochroman (5) (40%) (Scheme 1). The structure of (4) was assigned on the basis of its simple ^1H n.m.r. spectrum while (5) was identical with material synthesised earlier from 3-pentafluorophenylpropanoic acid,[8] which on reduction with BH_3–tetrahydrofuran gave 3-pentafluorophenylpropan-1-ol. With HBr this gave 1-bromo-3-pentafluorophenylpropane, which on treatment with thiourea gave an *S*-thiouronium salt (not isolated). Hydrolysis with sodium hydroxide in dilute solution gave the thiochroman (5) (21%).

The formation of (4) and (5) from (1) has a precedent in the hydrocarbon system phenyl prop-2-enyl sulphide, which in quinoline gave approximately equal proportions of the non-fluorine-containing analogues of (4) and (5) *via* 2-(prop-2-enyl)thiophenol,[9] cyclisation reactions which in another system have been shown to proceed *via* competing electrophilic and radical mechanisms respectively.[10]

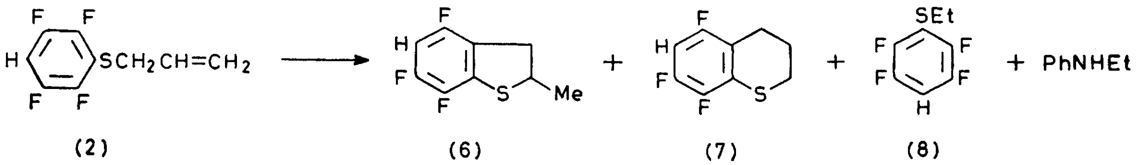


(4) (5)

SCHEME 1

The reaction of prop-2-enyl 2,3,5,6-tetrafluorophenyl ether (2) in refluxing *NN*-diethylaniline for 190 h gave three neutral products after removal of nitrogen-containing base materials with acid: 4,6,7-trifluoro-2,3-dihydro-2-methyl-1-benzothiophen (6) (5%), 5,7,8-trifluorothiochroman (7) (12%), and ethyl 2,3,5,6-tetrafluorophenyl sulphide (8) (18%); the residue was tarry intractable material. The structures of (6) and (7) were assigned on the basis of their simple ^1H n.m.r. spectra (which indicated the fused-ring structures) and their ^{19}F n.m.r. spectra which showed the presence of only three fluorine atoms in each compound. The sulphide (8) was identical with material synthesised from

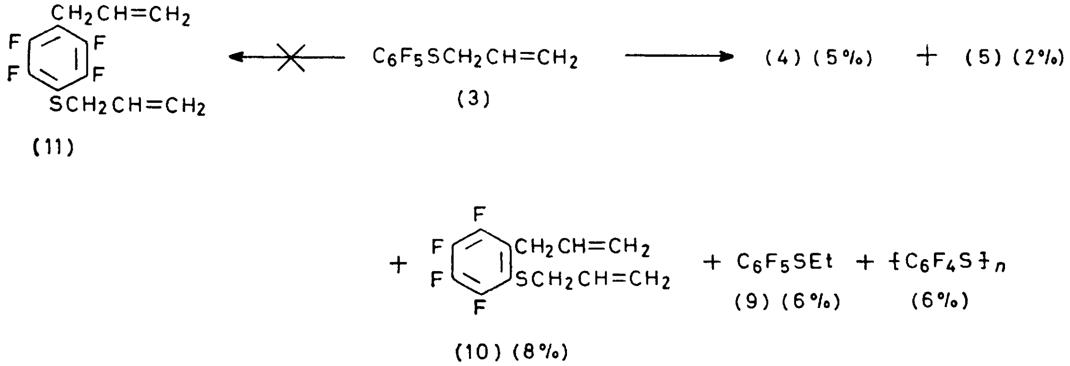
2,3,5,6-tetrafluorothiophenol by treatment with n-butyl-lithium and ethyl iodide. In an experiment designed to evaluate the possible role of the solvent in the reaction, the sulphide (2) when treated with 0.5 mol equiv. of *NN*-diethylaniline gave *N*-ethylaniline (20%). The overall reaction of (2) is shown in Scheme 2.



SCHEME 2

Pentafluorophenyl prop-2-enyl sulphide (3) was recovered unchanged under both sets of conditions which brought about reaction with the corresponding ether: (a) a vapour-phase reaction at 250 °C over 19 h; [2] and (b) when distilled *in vacuo* through a quartz tube packed with silica wool at 370 °C,[2] although at 465 °C decomposition occurred to give pentafluorothiophenol and unidentified volatile materials. No reaction occurred in refluxing n-decane but a complex range of products was obtained after 23 h in each case in refluxing *NN*-diethylaniline, quinoline, and dimethyl sulphoxide. *NN*-Diethylaniline was chosen for larger-scale experiments as this effected the largest extent of reaction, although much intractable material was also produced.

The crude product from (3) after treatment with acid to remove solvent and other nitrogen-containing base materials was shown to contain at least fourteen products by g.l.c. in addition to polymeric perfluoropoly(phenylene sulphide),[7] and was partially separated by fractional distillation followed by chromatography on silica and g.l.c. Four components were isolated and identified by comparison with materials prepared by other routes. These were 4,5,6,7-tetrafluoro-2,3-dihydro-2-methyl-1-benzothiophen (4) and 5,6,7,8-tetrafluorothiochroman (5) described earlier, ethyl pentafluorophenyl sulphide (9), and prop-2-enyl 3,4,5,6-tetrafluoro-2-(prop-2-enyl)phenyl sulphide (10). Compound (9) was synthesised from pentafluorothiophenol by treatment with n-butyl-lithium and ethyl iodide; compound (10) was obtained from 2,3,4,5-tetrafluorothiophenol by consecutive reactions with n-butyl-lithium, copper(I) chloride, and prop-2-enyl bromide.[11] Prop-2-enyl 2,3,5,6-tetrafluoro-4-(prop-2-enyl)phenyl sulphide (11) was prepared in a similar way to compound (10) using 2,3,5,6-tetrafluorothiophenol. An estimation of the yields of the identified products was carried out by g.l.c. using a gas-density balance detector. The results are shown in Scheme 3, in an analysis which also excluded (11) as a reaction product.

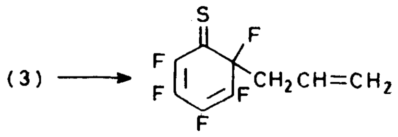


SCHEME 3

We have endeavoured to identify the structures of some of the ten remaining components by considering what other products could possibly be formed from (3), and the solvent *NN*-diethylaniline which is both a base and a nucleophile, and attempting their syntheses. As a base the possibility existed for proton abstraction from the prop-2-enylthio-group $(\longrightarrow \text{S}\bar{\ddot{\text{C}}}\text{H–CH=CH}_2 \longleftrightarrow \text{–S–CH=CH–}\bar{\ddot{\text{C}}}\text{H}_2)$ with the terminal carbon subsequently effecting an intramolecular nucleophilic displacement of fluorine from the aromatic ring to give 5,6,7,8-tetrafluoro-2*H*-1-benzothiopyran. However, this product was not formed in the reaction of (3) with the powerful base sodium hydride in refluxing tetrahydrofuran over 5 h. The starting material was recovered unchanged, although there still remains the possibility of reaction at higher temperatures, so that the presence of the benzothiopyran cannot be totally excluded from the reaction in refluxing *NN*-diethylaniline.

NN-Diethylaniline as a nucleophile could possibly displace the 4-fluorine in (3) [12] and the resulting quaternary ammonium salt could be de-*N*-ethylated by fluoride ion to give $1,4\text{-PhN(Et)C}_6\text{F}_4\text{SCH}_2\text{CH=CH}_2$. The attempted synthesis of this compound from (3) and PhN(Et)Li in dioxan at reflux temperature over 5 h did not bring about any displacement of fluorine, so it was concluded that *NN*-diethylaniline would also be an ineffective nucleophile.

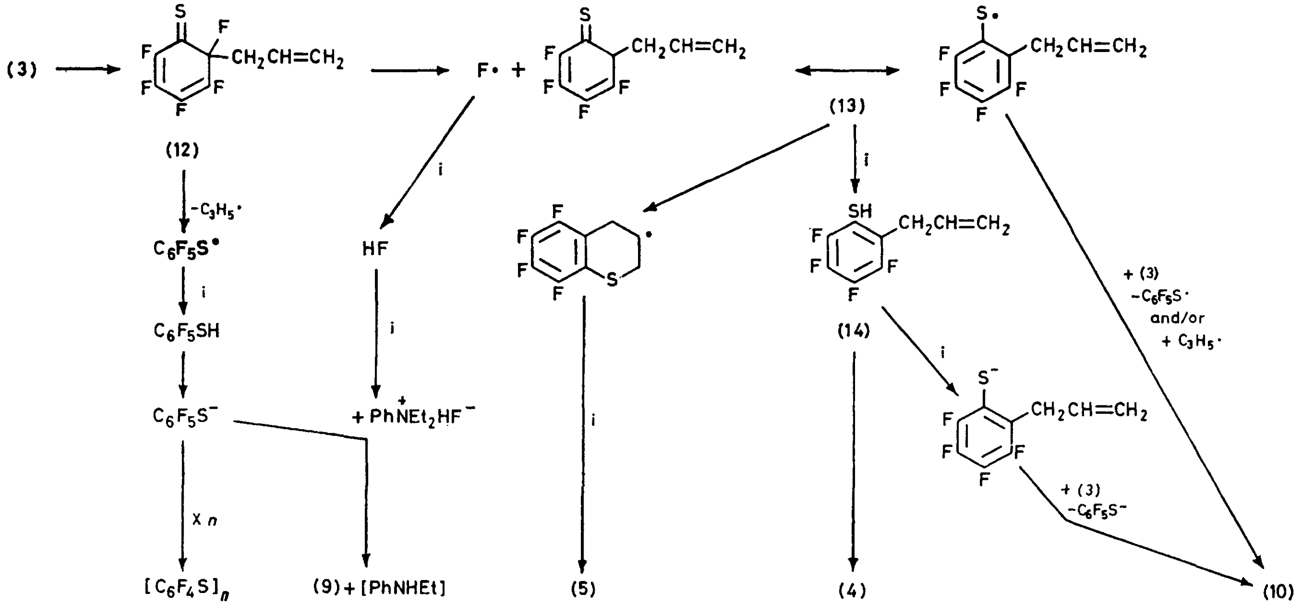
The conversions of compound (2) into (6) and (7) (Scheme 2) and of compound (3) into (4) and (5) (Scheme 3) formally require the loss of one fluorine and the gain of one hydrogen in the products, while the formation of (10) from (3) requires the overall replacement of a fluorine by a prop-2-enyl group, reactions which to our knowledge have no precedent. The only system which has been investigated which contained halogen atoms in an aromatic ring *ortho* to a prop-2-enyl thio-group is the 2,3,5,6-tetrachloro-4-pyridyl compound [13] and only intractable products were obtained on thermolysis.



(12)

Scheme 4

The specific formation of overall *ortho*-fluorine substitution products in the reactions of (2) and (3) indicates that the three-carbon prop-2-enyl chain becomes displaced to the site *ortho* to sulphur by the expected [3,3] sigmatropic shift, illustrated in Scheme 4 with pentafluorophenyl prop-2-enyl sulphide (3). The observation that no product containing the *para*-(prop-2-enyl) group is found in this reaction [specifically, there is none of compound (11), even though its isomer (10) is present] or in the reaction involving (2), is evidence for the absence of a Cope rearrangement following the initial Claisen rearrangement. Moreover a nucleophilic displacement of fluorine is ruled out since this process would displace the *para*-fluorine in (3).[12]



Scheme 5 *Reagent:* i, PhNEt$_2$

It has been shown that hexabromocyclohexa-2,5-dienone is an electrophilic brominating agent,[14] so the possibility that the aliphatic C–F in (12) could be displaced effectively as F$^+$ was considered, which would lead to electrophilic substitution of hydrogen in the solvent. However this possibility has been excluded since ^{19}F n.m.r. failed to detect any fluorine in recovered *NN*-diethylaniline.

Recently the thermal rearrangement reaction of prop-2-enyl 2,3,5,6-tetrachloro-4-pyridyl ether in sulpholan at 190 °C has been reported.[13] Among the several reaction products isolated was 4,6,7-trichloro-2,3-dihydro-2-methylfuro[3,2-*c*]pyridine [closely related in structure to (4) and (6)], the formation of which was rationalised on the basis of an initial [3,3] sigmatropic rearrangement followed by homolytic cleavage of the aliphatic C–Cl bond; other products arose by the competing loss of the prop-2-enyl radical from the same carbon atom. The remarkable formation of the fluorine-displacment products from (2) and (3) described in this paper can be rationalised in terms of an analogous mechanism which demands the homolytic fission of an aliphatic C–F bond from the corresponding Claisen rearrangement intermediate, and is illustrated in Scheme 5 for pentafluorophenyl prop-2-enyl sulphide (3). Loss of a fluorine atom from (12) gives the radical (13) which can react in a number of ways. Cyclisation and hydrogen abstraction from the solvent gives (5). Alternatively the intermediate (13) can abstract hydrogen from the solvent to form the thiol (14) which in turn can cyclise to (4) by an electrophilically induced reaction mechanism.[10] Compound (10) could be formed either by an S_N2' displacement of $C_6F_5S^-$ from (3) *via* the thiolate from (14), or by the related displacement of $C_6F_5S\cdot$ from (3) *via* (13). Further reaction of $C_6F_5S\cdot$ with solvent would give C_6F_5SH and then $C_6F_5S^-$ which would polymerise to perfluoropoly(phenylene sulphide). The fluorine atom is presumed to abstract hydrogen from the solvent to give HF which is immediately neutralised by *NN*-diethylaniline to give the quaternary ammonium fluoride. Reaction of this salt with $C_6F_5S^-$ will give (9) and an equivalent amount of *N*-ethylaniline. No attempt was made to isolate this secondary amine from this particular reaction, although it was found in the reaction involving prop-2-enyl 2,3,5,6-tetrafluorophenyl sulphide (2), accompanied by an almost equivalent amount of ethyl 2,3,5,6-tetrafluorophenyl sulphide (8) for which a similar scheme is applicable. The analogue of compound (10) was not found in the reaction with (2). Scheme 5 also shows an alternative decomposition path for (12): loss of the prop-2-enyl radical [which could be captured by (13) to give (10)] and subsequent reactions of $C_6H_5S^{\bullet}$ described before. The fate of the amine residue after each hydrogen abstraction reaction is not known, but could possibly proceed to vinylamines which could polymerise.*

The particular feature of interest in this proposed reaction mechanism is the low temperature ($\leqslant$220 °C) which is necessary to effect homolytic fission of the aliphatic C–F bond. Presumably one of the driving forces for the reaction is the stability of the radical formed as a result of extended conjugation, which is adequate in the case of the one formed from the cyclohexa-2,4-dienethione intermediate, *e.g.* (13), but insufficient for the corresponding oxygen compound since pentafluorophenyl prop-2-enyl ether gives products which arise from the formation of internal Diels–Alder addition reactions of the intermediate cyclohexa-2,4-dienone rather than reacting by loss of a fluorine atom.[2] However, the radical reactions of the intermediate produced by the thermal rearrangement of prop-2-enyl 2,3,5,6-tetrachloro-4-pyridyl ether [13] must be a consequence of the weaker C–Cl bond since the corresponding tetrafluoro-compound gives only the internal Diels–Alder adduct from the intermediate.[3]

EXPERIMENTAL

Pentafluorophenyl Prop-2-enyl Sulphide (3).—Pentafluorothiophenol [7] (76.7 g) in dry tetrahydrofuran (THF) (700 ml) under nitrogen was treated at $\leqslant -70$ °C with n-butyl-lithium in hexane (320 ml; 1.28M) over 2 h, the last traces were washed in with more THF (100 ml), and prop-2-enyl bromide (52.9 g) in dry THF (100 ml) was added over 20 min at -70 °C. The mixture was allowed to warm to room temperature over 4 h, and was diluted with water (800 ml), acidified with hydrochloric acid (200 ml; 2M), and extracted with diethyl ether (3 × 300 ml). The extracts were dried ($MgSO_4$), the solvents were removed by distillation through a 3 ft column initially and the residue distilled *in vacuo* to give the *sulphide* (3) (81.4 g, 88%), b.p. 76 °C at 9.5 mmHg (Found: C, 45.2; H, 2.4. $C_9H_5F_5S$ requires C, 45.0; H, 2.1%); M^+, 240.

Prop-2-enyl 2,3,4,5-Tetrafluorophenyl Sulphide (1).—2,3,4,5-Tetrafluorothiophenol [6] was treated as described above to give the *sulphide* (1) (85%), b.p. 76—78 °C at 7 mmHg (Found: C, 48.9; H, 2.9. $C_9H_6F_4S$ requires C, 48.6; H, 2.7%); M^+, 222.

Prop-2-enyl 2,3,5,6-Tetrafluorophenyl Sulphide (2).—2,3,5,6-Tetrafluorothiophenol [7] was treated as described above to give the *sulphide* (2) (83%), b.p. 86—89 °C at 12.5 mmHg (Found: C, 48.9; H, 2.8. $C_9H_6F_4S$ requires C, 48.6; H, 2.7%); M^+, 222.

Ethyl Pentafluorophenyl Sulphide (9).—Pentafluorothiophenol was treated as described above but using ethyl iodide in place of prop-2-enyl bromide, to give the *sulphide* (9) (68%), b.p. 78—79 °C at 14 mmHg (Found: C, 42.3; H, 2.4. $C_8F_5H_5S$ requires C, 42.1; H, 2.2%); M^+, 228.

Ethyl 2,3,5,6-Tetrafluorophenyl Sulphide (8).—2,3,5,6-Tetrafluorothiophenol was treated as in the previous experiment to give the sulphide (8) (76%), b.p. 87—88 °C at 11 mmHg (Found: C, 45.5; H, 3.2. $C_8H_6F_4S$ requires C, 45.7; H, 2.9%); M^+, 210.

Prop-2-enyl 3,4,5,6-Tetrafluoro-2-(prop-2-enyl)phenyl Sulphide (10).—2,3,4,5-Tetrafluorothiophenol (4.92 g) in dry THF (200 ml) was treated at $\leqslant -70$ °C with n-butyl-lithium in hexane (42 ml; 1.32M) under nitrogen over 30 min. The mixture was stirred with copper(I) chloride (5.8 g) at -76 °C for 5 h, warmed to 0 °C, and prop-2-enyl bromide (10.2 g) added at <10 °C. After 14.5 h at room temperature, an excess of aqueous ammonia (2M) was added to the mixture which was then extracted with diethyl ether. The extracts were washed with hydrochloric acid (2M), dried ($MgSO_4$), the solvent evaporated, and the residue distilled *in vacuo* to give two fractions at 0.05 mmHg: (a) (3.02 g), b.p. 43—57 °C, a mixture of the product and an unidentified material; and (b) (2.64 g), b.p. 57—59 °C, which was largely the product (by g.l.c.). The pure *sulphide* (10) was obtained by preparative scale g.l.c. using a column packed with 30% silicone elastomer operated at 200 °C (Found: C, 55.2; H, 4.0. $C_{12}H_{10}F_4S$ requires C, 55.0; H, 3.8%); M^+, 262.

Prop-2-enyl 2,3,5,6-Tetrafluoro-4-(prop-2-enyl)phenyl Sulphide (11) —2,3,5,6-Tetrafluorothiophenol was treated as in the previous experiment, only with copper(I) iodide being used in place of the chloride, to give the *sulphide* (11) (71%), b.p. 66—70 °C at 0.05 mmHg (Found: C, 55.1; H, 4.2. $C_{12}H_{10}F_4S$ requires C, 55.0; H, 3.8%); M^+, 262.

3-*Pentafluorophenylpropan*-1-*ol*.—3-Pentafluorophenylpropanoic acid [8] (14.45 g) in dry THF (150 ml) was treated at *ca.* 20 °C with BH_3–THF (90 ml; 0.86M) under nitrogen over 30 min. The mixture was kept at room temperature for 3 h, the excess of hydride was destroyed by adding water, and, after acidification, the solution was extracted with diethyl ether. The extracts were dried ($MgSO_4$), the solvents were evaporated, and the residue was

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* The reason for proposing *homolytic* fission of the carbon–halogen bond in intermediates described in this work and in that cited earlier (ref. 13) lies solely in the isolation of hydrogen abstraction products. No such products were found in our work with pentafluorophenyl and 1,3,4,5,6,7,8-heptafluoronaphthyl *prop-2-ynyl* ethers (ref. 1), though they had been isolated in earlier work with such ethers blocked by halogen (chlorine and bromine) in the *ortho*-positions. Consequently, both homolytic *and* heterolytic fission of the aliphatic C–F bond in the intermediates formed from these polyfluoroaryl prop-2-ynyl ethers were proposed and no decision was taken as to which mechanism was operative (ref. 1). *If* heterolytic fission of the C–F bond in (12) did take place, then the cationic species formed would require hydride ion (H^-) abstraction from the solvent at some stage to give compounds (4) and (5), and the formation of (10) would require displacement of $C_6F_5S^+$ from (3), or capture of $C_3H_5^-$ as a result of a competing heterolytic cleavage reaction of (12). To our knowledge, none of these reactions has a precedent and so are discounted.

distilled *in vacuo* to give the *alcohol* (9.96 g), b.p. 113 °C at 12 mmHg (Found: C, 48.0; H, 3.3. $C_9H_7F_5O$ requires C, 47.8; H, 3.1%).

1-*Bromo*-3-*pentafluorophenylpropane*.—The foregoing alcohol (9.96 g), treated with hydrobromic acid (25 ml; 46% w/w) and sulphuric acid (5 ml; 18M) for 18.5 h at reflux temperature gave the *bromo-compound* (10.39 g), b.p. 102—104 °C at 11 mmHg (Found: C, 37.5; H, 2.3. $C_9H_6BrF_5$ requires C, 37.4; H, 2.1%).

5,6,7,8-*Tetrafluorothiochroman* (5).—The foregoing bromo-compound (4.14 g) and thiourea (1.71 g) were heated together in ethanol (30 ml) under reflux for 64 h. The solvent was evaporated off, water (20 ml) was added, and the solution was poured into sodium hydroxide solution [1.2 g in water (300 ml)]. The mixture was boiled for 5 h and extracted with diethyl ether, the extracts were dried ($MgSO_4$), and the solvent was evaporated. Distillation of the residue *in vacuo* gave a mixture (0.95 g), b.p. 34—72 °C at 0.05 mmHg, of (5) [*ca.* 70% (g.l.c.)] and an unidentified compound. Preparative g.l.c. of this mixture (30% silicone elastomer at 200 °C), followed by preparative t.l.c. on silica with light petroleum (b.p. 40—60 °C) as solvent on the enriched material gave the pure *thiochroman* (5) (0.174 g), b.p. 42—56 °C at 0.05 mmHg (Found: C, 48.9; H, 2.8. $C_9H_6F_4S$ requires C, 48.6; H, 2.7%); M^+, 222; δ_F ($CDCl_3$) 143.6, 145.8, 162.5, and 165.5 p.p.m. upfield from external $CFCl_3$; δ_H ($CDCl_3$) 2.14, 2.74, and 2.96 (each m, 3 × CH_2).

Thio-Claisen Rearrangement of Prop-2-*enyl* 2,3,4,5-*Tetrafluorophenyl Sulphide* (1).—The sulphide (1) (5.05 g) and *NN*-diethylaniline (50 ml) were heated under reflux for 23 h. The mixture was acidified with hydrochloric acid (2M) and extracted with diethyl ether, the extracts were dried ($MgSO_4$), and the solvent was evaporated off. The residue was distilled *in vacuo* to give a liquid (4.07 g), b.p. $\leqslant$100 °C at 0.05 mmHg, which contained three components (g.l.c. on a column coated with 2-cyanoethyl methyl silicone, at 200 °C). Chromatography of this mixture on silica [190 × 2.4 cm column, light petroleum (b.p. 40—60 °C) as eluant] gave two fractions: (i) a mixture of two components (g.l.c.), followed by (ii), 5,6,7,8-tetrafluorothiochroman (5) (2.00 g), identified by its i.r. spectrum. Fraction (i) was separated by preparative g.l.c. (2-cyanoethyl methyl silicone column at 200 °C) to give two fractions, (a) and (b). Fraction (b) was 4,5,6,7-*tetrafluoro*-2,3-*dihydro*-2-*methyl*-1-*benzothiophen* (4) (0.91 g), b.p. 40—45 °C at 0.05 mmHg (Found: C, 48.9; H, 2.8. $C_9H_6F_4S$ requires C, 48.7; H, 2.7%); M^+, 222; δ_H ($CDCl_3$) 1.48 (d, CH_3), 3.01—3.46br (m, CH_2), and 4.12 (m, CH). Fraction (a) (1.08 g) was a mixture of (4) and a shorter retained (g.l.c.) compound which was not identified, in approximately equal amounts.

Reactions in NN-*Diethylaniline*.—(a) *Pentafluorophenyl prop*-2-*enyl sulphide* (3). The sulphide (3) (24.1 g) and *NN*-diethylaniline (240 ml) were heated under reflux for 23 h under nitrogen. The mixture was treated with an excess of hydrochloric acid (4M), polymeric perfluoropoly(phenylene sulphide) [7] (1.37 g) was filtered off, and the filtrate was extracted with diethyl ether. The extracts were dried ($MgSO_4$), the solvent was evaporated off, and the residue, shown to contain at least fourteen components by g.l.c. on 2-cyanoethyl methyl silicone at 200 °C, was distilled *in vacuo* through a 6-in concentric-column fractionating column. Fourteen fractions were collected.

Fractions 1—3 (8.23 g), b.p. 76—81.5 at 13 mmHg, contained *ca.* 80% unchanged sulphide (3). In a separate experiment both this material (3) and ethyl pentafluorophenyl sulphide (9) were separated by preparative g.l.c. on 2-cyanoethyl methyl silicone at 160 °C and identified by i.r. spectroscopy.

Fractions 4—11 (5.91 g) had b.p. 19—80 °C at 0.05 mmHg. The components of fractions 4—6 (1.91 g) were partially separated by preparative t.l.c. on silica [light petroleum (b.p. 40—60 °C) as eluant] to give 4,5,6,7-tetrafluoro-2,3-dihydro-2-methyl-1-benzothiophen (4) (0.33 g) identified by its i.r. spectrum; the components of fractions 9 and 10 (3.1 g) were partially separated by repeated g.l.c. (on 2-cyanoethyl methyl silicone at 200 °C) to give prop-2-enyl 3,4,5,6-tetrafluoro-2-(prop-2-enyl)phenyl sulphide (10) (0.39 g), identified by i.r. spectroscopy.

Fractions 12—14 (0.82 g) had b.p. 44—95 °C at 0.001 mmHg. The components of fractions 12 and 13 (0.25 g) were partially separated by preparative t.l.c. on silica [light petroleum (b.p. 40—60 °C) as eluant] to give 5,6,7,8-tetrafluorothiochroman (5) (0.043 g) identified by its i.r. spectrum. Involatile material amounted to 8.4 g.

G.l.c. of the distilled product, using a gas-density balance detector in conjunction with a 30% silicone elastomer column at 200 °C, indicated the yields of the various compounds identified in the reaction to be: (10), *ca.* 8%; (4), *ca.* 5%; (5), *ca.* 2%; and (9), *ca.* 6%. Perfluoropoly(phenylene sulphide) accounted for 6% of the product.

(b) *Prop*-2-*enyl* 2,3,5,6-*Tetrafluorophenyl Sulphide* (2).—The sulphide (2) (4.91 g) and *NN*-diethylaniline (50 ml) were heated under reflux for 190 h under nitrogen. The mixture was diluted with diethyl ether, washed with an excess of hydrochloric acid (4M), and the organic layer was separated and dried ($MgSO_4$). Evaporation gave a residue which appeared to contain only two components {t.l.c. [silica; light petroleum (b.p. 40—60 °C) as eluant]}. However, g.l.c. (2-cyanoethyl methyl silicone at 208 °C) revealed the presence of four components, one of which was unchanged starting material (2). Chromatography of the mixture on silica (190 × 2.4 cm column) using light petroleum (b.p. 40—60 °C) as eluant gave two fractions: (i) a mixture of three components (g.l.c.) (3.58 g) one of which was (2); and (ii) 5,7,8-*trifluorothiochroman* (7) (0.52 g), m.p. 45.5—46.5 °C [from light petroleum (b.p. 30—40 °C)] (Found: C, 52.9; H, 3.1. $C_9H_7F_3S$ requires C, 52.9; H, 3.4%); M^+, 204; δ_F ($CDCl_3$) 120.6, 139.0, and 144.7 p.p.m. upfield from internal $CFCl_3$; δ_H ($CDCl_3$) 2.14, 2.78, and 3.01 (each m, 3 × CH_2), and 6.64 (m, aromatic).

Fraction (i) was treated with an excess of BH_3–THF (20 ml; 2M) under nitrogen at 20 °C for 1 h [to convert unchanged (2) into a trialkylborane which was immobile on chromatography on silica–light petroleum], and the excess of hydride was destroyed at 0 °C with water. The mixture was acidified with hydrochloric acid (2M) and extracted with diethyl ether. The extracts were dried ($MgSO_4$), the solvent was evaporated, and the residue was separated into its two components by preparative g.l.c. (2-cyanoethyl methyl silicone at 185 °C). The first component was ethyl 2,3,5,6-tetrafluorophenyl sulphide (8) (0.84 g), identified by its i.r. spectrum; the second component was 4,6,7-*trifluoro*-2,3-*dihydro*-2-*methyl*-1-*benzothiophen* (6) (0.24 g), b.p. 44—50 °C at 0.05 mmHg (Found: C, 52.8; H, 3.7. $C_9H_7F_3S$ requires C, 52.9; H, 3.4%); M^+, 204; δ_F ($CDCl_3$) 117.9, 136.1, and 143.7 p.p.m. upfield from external $CFCl_3$; δ_H ($CDCl_3$) 1.49 (d, CH_3), 2.98—3.41br (m, CH_2), 4.14 (m, aliphatic CH), and 6.57 (m, aromatic CH).

In a separate experiment, compound (2) (4.92 g) and *NN*-diethylaniline (1.55 g) were heated in a sealed tube at 210 °C for 22 h. The mixture was diluted with diethyl ether and washed with hydrochloric acid (2M). The acid extracts were treated with an excess of sodium hydroxide (2M), the mixture was extracted with diethyl ether and the solvent was evaporated from the dried ($MgSO_4$) extracts. The residue was separated by repeated preparative t.l.c. on silica [CCl_4–$CHCl_3$ (2 : 1 v/v) as eluant] to give *N*-ethylaniline (0.25 g) identified by its i.r. spectrum.

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