

Partially Fluorinated Heterocyclic Compounds. Part 21.¹ Isomerisations of Pentafluorophenyl and 1,3,4,5,6,7,8-Heptafluoro-2-naphthyl Prop-2-ynyl Sulphides: Differing Courses of Reactions of the Naphthyl Sulphides and Ethers in Glass and Nickel Apparatus. Considerations of Mechanism

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Pentafluorophenyl prop-2-ynyl sulphide (**1**) has been isomerised to 4,5,6,7-tetrafluoro-2-fluoromethylbenzo[*b*]thiophene (**3**) in a liquid phase reaction while 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-ynyl sulphide (**2**) gave 4,5,6,7,8,9-hexafluoro-2-fluoromethylnaphtho[2,1-*b*]thiophene (**4**) in both liquid and vapour phase reactions. Compound (**1**) reacted with *p*-xylene at 180 °C to give 2-(2,5-dimethylbenzyl)-4,5,6,7-tetrafluorobenzo[*b*]thiophene (**5**), which was also formed from (**3**), *p*-xylene, and BF₃-diethyl ether at 25 °C. The sulphide (**2**) reacted with benzene and with *p*-xylene, at 160 °C, to give the 2-benzyl- and 2-(2,5-dimethylbenzyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-*b*]thiophene compounds (**7**) and (**8**) respectively; (**7**) and (**8**) were also formed from (**4**), with benzene and *p*-xylene respectively and BF₃-diethyl ether. At 160 °C in nickel apparatus, the 2-fluoromethyl compound (**4**) was shown to be an intermediate in the conversion of (**2**) into (**8**) with *p*-xylene. At 140 °C in nickel apparatus, (**2**) and *p*-xylene gave (**4**) as the major product whereas in glass apparatus only (**8**) was formed. The glass surface of the reaction vessel acted as a Lewis acid catalyst at elevated temperatures, an effect which was also observed in the reactions of 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-ynyl ether (**9**) with *p*-xylene and isopropylbenzene at 140 °C; the aromatic substitution products (**10**) and (**14**) respectively were formed, whereas in nickel apparatus, the 2-fluoromethyl compound (**11**) was the main product in both reactions. Compound (**11**) reacted with *p*-xylene in glass apparatus at 140 °C to give (**10**) exclusively; in *N,N*-diethylaniline at 140 °C, (**11**) was recovered unchanged.

Charge-separated species (**19**) and (**25**) are proposed as intermediates in the reactions of the ether (**9**) and sulphide (**2**) via the heterolytic fission of the sp³ C-F bond in the Claisen rearrangement intermediates (**13**) and (**24**) respectively. The isomerisations of (**2**) and (**9**) therefore, proceed via reactions which include '1,4'-fluorine shifts which occur via ionic mechanisms.

Pentafluorophenyl prop-2-ynyl sulphide has been shown in earlier work to give a complex mixture of products when heated in *N,N*-diethylaniline under reflux, the intermediacy of the *ortho*-Claisen rearrangement product being invoked to account for the five materials actually identified.² Here we report the preparation and some thermally induced reactions of pentafluorophenyl and 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-ynyl sulphides (**1**) and (**2**) respectively and some reactions of 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-ynyl ether (**9**) with aromatic compounds, reactions which had previously been carried out in glass apparatus but which have now been repeated in nickel apparatus. The course of these reactions and some related chemistry using 4,5,6,7,8,9-hexafluoro-2-fluoromethylnaphtho[2,1-*b*]furan (**11**) has enabled considerable progress to be made concerning the mechanistic aspects of the further reactions of the Claisen rearrangement products derived from polyfluoroaryl prop-2-ynyl ethers and sulphides.

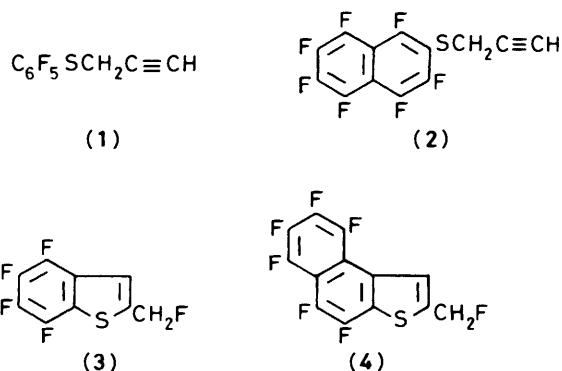
Results and Discussion

Treatment of pentafluorothiophenol in tetrahydrofuran at -70 °C with *n*-butyl-lithium, followed by the addition of prop-2-ynyl bromide gave pentafluorophenyl prop-2-ynyl sulphide (**1**) (71%). 1,3,4,5,6,7,8-Heptafluoro-2-naphthyl prop-2-ynyl ether (**2**) was prepared in 64% yield by first treating perfluoronaphthalene with sodium hydrosulphide in a mixture of ethylene glycol and dimethylformamide at -55 °C and then adding prop-2-ynyl bromide without prior isolation of the 2-thiol compound.

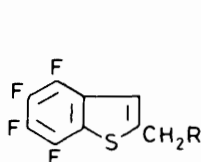
When pentafluorophenyl prop-2-ynyl sulphide (**1**) was

heated in CF₂ClCFCl₂ in a nickel tube at 180 °C for 91 h a low yield (13%) of 4,5,6,7-tetrafluoro-2-fluoromethylbenzo[*b*]thiophene (**3**) was obtained. While the isomerisation of the naphthalene compound (**2**) in the Freon solvent in a nickel tube at 160 °C for 24 h was a more efficient reaction in giving the 2-fluoromethyl derivative (**4**) (41%), an even more successful reaction resulted from the distillation of (**2**) *in vacuo* through a silica tube packed with quartz wool at 360 °C: compound (**4**) was obtained in 81% yield. The ¹⁹F n.m.r. spectrum of compound (**4**) had only one *peri*J_{F,F} coupling constant (66 Hz) which showed that the fluorine at C-1 in (**2**) had been displaced.

Pentafluorophenyl prop-2-ynyl sulphide (**1**) gave such a complex mixture of products when heated with benzene in a nickel tube at 180 °C for 96 h that no attempt was made to

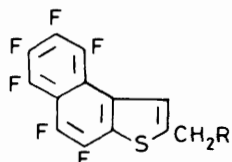


isolate any of the components. However, with *p*-xylene under the same conditions, the sulphide (1) gave 2-(2,5-dimethylbenzyl)-4,5,6,7-tetrafluorobenzo[*b*]thiophene (5) in low yield (7%). Compound (5) was prepared efficiently (94% yield) by an alternative procedure which involved treating a mixture of the 2-fluoromethyl compound (3) in *p*-xylene with BF₃-diethyl ether at 25 °C for 150 min. In a similar manner, 2-benzyl-4,5,6,7-tetrafluorobenzo[*b*]thiophene (6) (93%) was prepared from (3) and benzene.



(5) R = C₆H₃Me₂ - 2, 5

(6) R = Ph



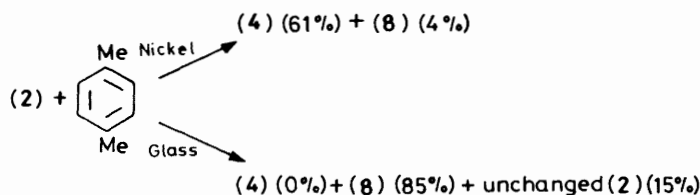
(7) R = Ph

(8) R = C₆H₃Me₂ - 2, 5

1,3,4,5,6,7,8-Heptafluoro-2-naphthyl prop-2-ynyl sulphide (2) gave a low yield of 2-benzyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-*b*]thiophene (7) (16%) when heated with benzene in a nickel tube at 160 °C for 25 h. A similar reaction between the sulphide (2) and *p*-xylene gave 2-(2,5-dimethylbenzyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-*b*]thiophene (8) (51%). Again, the alternative procedure involving the treatment of the 2-fluoromethyl compound (4) in benzene and in *p*-xylene with BF₃-diethyl ether at 25 °C for 15 min gave compounds (7) (89%) and (8) (87%) respectively.

We discovered that when the duration of the reaction between 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-ynyl sulphide (2) and *p*-xylene in a nickel tube at 160 °C is reduced, the 2-fluoromethyl compound (4) is formed in addition to compound (8). Indeed, a semi-kinetics study of this reaction using ¹H and ¹⁹F n.m.r. spectroscopy to determine the relative proportions of the products showed that the 2-fluoromethyl compound (4) was actually an intermediate in the reaction.

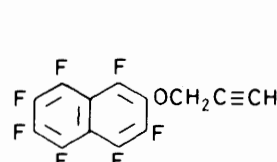
A vital observation was made for the reaction between 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-ynyl sulphide (2) and *p*-xylene. The nature of the product depended on whether the reaction was carried out in a nickel tube or in glass apparatus. The results for both experiments carried out at 140 °C over 24 h are shown in Scheme 1, and demonstrate



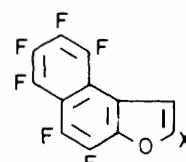
Scheme 1.

clearly that the glass is functioning as an efficient Lewis acid in some way along the reaction pathway. In view of this discovery it became imperative to re-examine some of our earlier work with 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-ynyl ether (9)³⁻⁵ and also compare the results with the same reactions carried out in nickel apparatus.

1,3,4,5,6,7,8-Heptafluoro-2-naphthyl prop-2-ynyl ether (9) was heated with *p*-xylene under reflux in glass apparatus at 140 °C for 20 h and gave 2-(2,5-dimethylbenzyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-*b*]furan (10) (62%) as was found



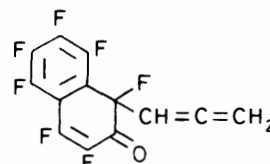
(9)



(10) X = CH₂C₆H₃Me₂ - 2, 5

(11) X = CH₂F

(12) X = CH₂⁺



(13)

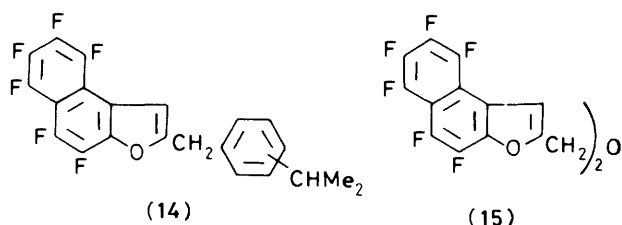
previously;³ no 4,5,6,7,8,9-hexafluoro-2-fluoromethylnaphtho[2,1-*b*]furan (11) was detected by ¹H or ¹⁹F n.m.r. in the reaction product. However, when the reaction was carried out in a nickel tube under identical conditions, the 2-fluoromethyl compound (11) was the major product (48%); the 2-(2,5-dimethylbenzyl) derivative (10) was present only to the extent of 5%. We also heated the 2-fluoromethyl compound (11) with *p*-xylene under reflux in glass apparatus at 140 °C for 20 h. No unchanged starting material remained at the end of the experiment; the product was the 2-(2,5-dimethylbenzyl) derivative (10) (78%). The reaction of (11) with *p*-xylene could also be brought about even more effectively at 25 °C by means of BF₃-diethyl ether over 150 min; compound (10) was formed in 98% yield. The conclusion drawn from these experiments is that once again the glass at 140 °C is behaving as a Lewis acid catalyst, promoting the formation of a carbocation (12) of considerable inherent stability.

The production of naphtho[2,1-*b*]furan compounds from the ether (9) has been shown previously to involve the initial formation of the Claisen rearrangement product 1,3,4,5,6,7,8-heptafluoro-1,2-dihydro-1-propa-1,2-dienylnaphthalen-2-one (13).⁴ Consequently, the formation of mainly the 2-fluoromethyl compound (11) in the reaction of (9) with *p*-xylene in nickel apparatus implies that in the intervening period between the conversion of the naphthalenone (13) into the 2-fluoromethyl compound (11)—the process which from the mechanistic point of view is the most intriguing aspect of all the studies undertaken with prop-2-ynyl ethers—insufficient cationic character of the type represented by (12) is present for electrophilic substitution to take place with *p*-xylene to any significant extent.

The naphthalenone (13) has been treated with *p*-xylene in the presence of BF₃-diethyl ether, but no reaction occurred until the temperature was raised to 120 °C. At this temperature over 3 h, since 15% of the starting material was converted into compound (10), the Lewis acid could be exercising a modest catalytic effect during this reaction. The surface of a glass vessel could also act as a Lewis acid towards the intermediate naphthalenone (13) in the reaction of the ether (9) with *p*-xylene in glass at the higher working temperature (140 °C), so that *in glass*, it is not possible to say categorically that the 2-fluoromethyl compound (11) is a definite intermediate in the formation of the *p*-xylene substitution product (10).

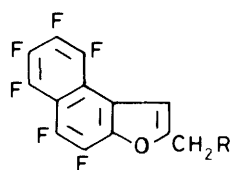
A conclusion to be drawn from the studies of the thermolyses of 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-ynyl ether (9) in *p*-xylene is that all those aromatic compounds which gave aromatic substitution products with (9) when the experiment was conducted in glass (benzene,³ isopropylbenzene⁴ and *N,N*-

diethylaniline⁵), should primarily give 4,5,6,7,8,9-hexafluoro-2-fluoromethylnaphtho[2,1-*b*]furan (**11**) when performed in nickel apparatus. In order to make a true comparison of these two possible courses of reaction, we re-investigated the thermolysis of the ether (**9**) and isopropylbenzene in a glass Carius tube at 143 °C for 24 h and analysed the crude reaction product by ¹H and ¹⁹F n.m.r. spectroscopy for the two products isolated previously;⁴ the naphthalenone (**13**) and the mixture of furan derivatives (**14**). Both were present, in the ratio of 6 parts of (**13**):94 parts of (**14**); there was no 2-fluoromethyl compound (**11**) in the mixture. However, when the reaction was carried out under identical conditions in nickel apparatus, the major product consisted of the 2-fluoromethyl compound (**11**) (65%) accompanied by the aromatic substitution product (**14**) (2%), and the ether compound (**15**) (14%) whose formation arose



from the failure to completely exclude water from the reacting system.⁴

The reaction of the ether (**9**) with *N,N*-diethylaniline had yielded the first sample ever made of the 2-fluoromethyl compound (**11**) (although only in 2% yield), so we repeated the reaction in a glass Carius tube under carefully controlled conditions at 140 °C for 24 h. The products obtained were the same as those obtained previously⁵ namely a mixture of two furan derivatives incorporating the *N,N*-diethylaniline residue (**16**) (23%); the 2-methyl derivative (**17**) (1%); and once again,



(16) R = C₆H₄NEt₂

(17) R = H

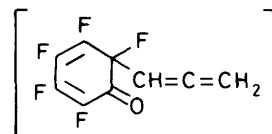
the 2-fluoromethyl compound (**11**) (2%). The surprising presence of (**11**) prompted the investigation of the stability of this compound in the nitrogen-containing solvent in glass apparatus.

4,5,6,7,8,9-Hexafluoro-2-fluoromethylnaphtho[2,1-*b*]furan (**11**) and *N,N*-diethylaniline were heated in a glass Carius tube at 140 °C for 24 h. The starting material was recovered unchanged to the extent of 97% which showed that the Lewis acid catalysing effect of the glass had been effectively neutralised—by the solvent performing its role as a base. This conclusion was confirmed by the observation that the reaction between (**11**) and *p*-xylene in glass, was completely inhibited when *N,N*-diethylaniline was added to the reaction mixture.* There remains, however, the rationalisation for the formation of the mixture of substitution products of *N,N*-diethylaniline, (**16**)

which were obtained from the reaction with 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-ynyl ether (**9**).

There is a problem regarding the mechanism of substitution of aromatic hydrogen in *N,N*-diethylaniline: neither homolytic nor Friedel-Crafts substitution reactions have ever been reported, though both processes in principle could account for the formation of (**16**). However, in the absence of a Lewis acid which would otherwise have converted a highly activating Et₂N-group into a highly deactivating quaternary ammonium substituent, an electrophilic substitution reaction provides a satisfactory rationalisation for the formation of the *N,N*-diethylaniline derivatives (**16**). During the transformation of the naphthalenone (**13**) to the 2-fluoromethyl compound (**11**) (the 2% formed in the reaction), sufficient cationic character must develop on the 2-CH₂ substituent of the furan ring during cyclisation for it to be captured to a major extent by the nucleophilic *N,N*-diethylaniline. With *p*-xylene and isopropylbenzene as the solvents in nickel apparatus (where no Lewis acid catalysing effects are operating), the fluoride ion is the more effective nucleophile, which accounts for the high proportions of the 2-fluoromethyl compound (**11**) formed in these reactions: 48% and 65% respectively. Using the Freon solvent CF₂ClCFCl₂, the ether (**9**) gave (**11**) in 81% yield.¹

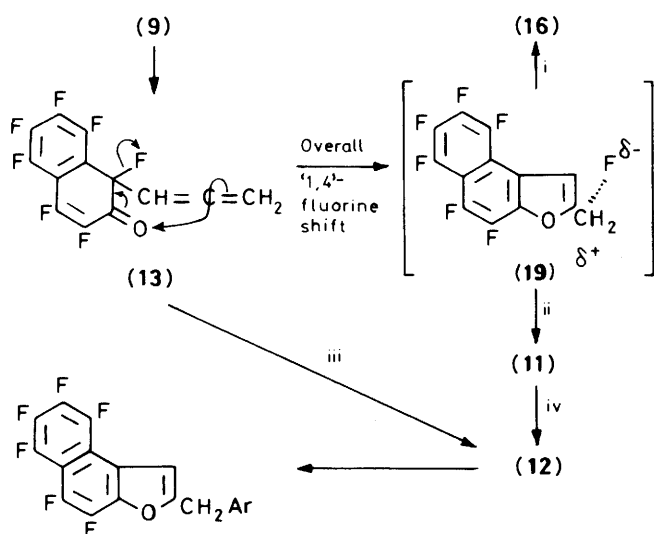
In an earlier paper,³ two mechanisms were proposed to account for the products formed in the thermolysis reactions of pentafluorophenyl prop-2-ynyl ether in the vapour phase and in aromatic solvents—reactions which were presumed to proceed *via* the Claisen rearrangement intermediate (**18**): (i) a homolytic cleavage of the sp³ hybridised C-F bond in (**18**), and (ii) a



(18)

heterolytic cleavage of this bond occurring synchronously with cyclisation. It is clear from the discussion concerning the reaction of the 2-naphthyl ether (**9**) with *N,N*-diethylaniline that the experimental evidence is consistent only with an intermediate having *some* degree of electrophilic character and, therefore, the heterolytic cleavage of the sp³ C-F bond in 1,3,4,5,6,7,8-heptafluoro-1,2-dihydro-1-propa-1,2-dienyl-naphthalen-2-one (**13**) is the only reasonable mechanism which allows for this, and contrasts with the free radical process which earlier had been proposed to account for the formation of products from the thermolysis of the closely related 1-chloro-(bromo)-2-naphthyl prop-2-ynyl ether.⁶ The ionic mechanism also provides a satisfactory explanation for the vapour phase isomerisations of pentafluorophenyl prop-2-ynyl ether to 4,5,6,7-tetrafluoro-2-fluoromethylbenzo[*b*]furan³ and of 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-ynyl ether (**9**) to 4,5,6,7,8,9-hexafluoro-2-fluoromethylnaphtho[2,1-*b*]furan (**11**)¹ where a pre-condition for the overall '1,4'-fluorine shifts, is that the fluorine should not depart very far from the organic moiety: the presence of charged species and their electrostatic attraction provides the necessary intimacy. Scheme 2 summarises our interpretation of the mechanistic aspects of some of the thermolysis reactions of 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-ynyl ether (**9**), with the charge separated species (**19**) being central to the hypothesis. It has been pointed out earlier that in the reaction of the ether (**9**) with *p*-xylene in glass apparatus, it is not possible to say whether the 2-fluoromethyl compound (**11**) is an intermediate because of the possible catalytic effect of the glass on the decomposition of

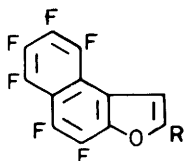
* We thank Professor A. R. Katritzky F.R.S. for suggesting this experiment.



Scheme 2. Reagents: i, PhNEt₂; ii, vapour phase; in nickel with *p*-xylene, Me₂CH or CF₂CICFCl₂; iii, BF₃-Et₂O-*p*-xylene; iv, in glass-*p*-xylene.

the naphthalenone (13). The same argument also applies to the related reactions involving benzene³ and isopropylbenzene.⁴

The preceding paper reported the reaction of the ether (9) with 3,3-dimethylbut-1-ene in a nickel tube at 150 °C for 20 h.¹ Alkene substitution products (20), (21), and (22) were the



(20) R = CH₂C(Me)₂C(Me)=CH₂

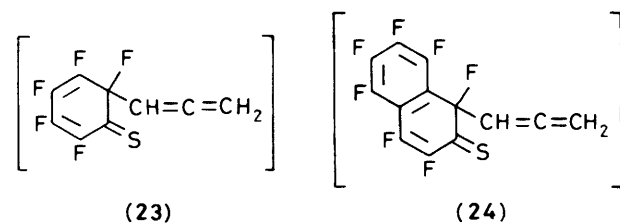
(21) R = CH=C(Me)CMe₃

(22) R = CH₂CH₂C(Me)=CMe₂

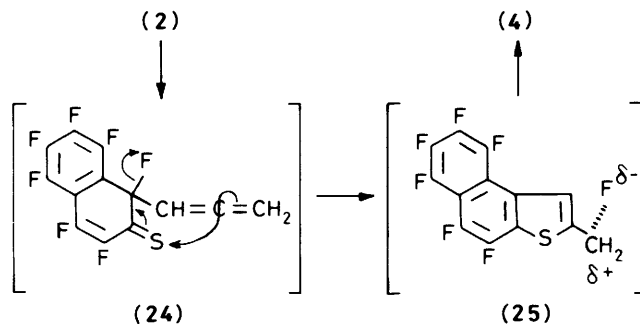
major products (37%), accompanied by a small amount of the 2-fluoromethyl compound (11) (3.5%). Moreover, under identical conditions in a nickel tube, the 2-fluoromethyl compound (11) was relatively unreactive towards 3,3-dimethylbut-1-ene, resulting in the recovery of 74% of the starting material and the formation of only 5% of a mixture of (20), (21), and (22). The reaction of the ether (9) with 3,3-dimethylbut-1-ene and with 2,3-dimethylbut-2-ene is entirely consistent with the intermediacy of the electrophilic species (19) in Scheme 2. The two alkenes behave in exactly the same way as does *N,N*-diethylaniline. Consequently cationic attack takes place initially on the alkenes when the ether (9) is one of the reactants.

It is not possible to define unambiguously the mechanism of cleavage of the CH₂-F bond in (11) in reactions with 3,3-dimethylbut-1-ene and with 2,3-dimethylbut-2-ene, in nickel apparatus.

Finally, we return to consider the thermolysis reactions of pentafluorophenyl and 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-ynyl sulphides (1) and (2) respectively; the allenic thiones (23) and (24) are the presumed intermediates formed during these reactions. The formation of 4,5,6,7,8,9-hexafluoro-2-fluoromethylnaphtho[2,1-*b*]thiophene (4) in the vapour



phase thermolysis of (2) can again be rationalised in terms of a heterolytic cleavage of the sp³ hybridised C-F bond in (24) leading to the dipolar species (25) (Scheme 3).



Scheme 3.

In nickel apparatus with *p*-xylene at 160 °C, reaction of the sulphide (2) first gave the 2-fluoromethyl compound (4) since the *p*-xylene is not sufficiently nucleophilic (compared with F⁻) to react with the weak electrophilic cation (25)—unlike its reaction with the formal 2-CH₂⁺ species formed from (4) and boron trifluoride-diethyl ether. The mechanism of the subsequent reaction of the 2-fluoromethyl compound (4) with *p*-xylene in nickel cannot be defined unambiguously. It is not possible to say whether the 2-fluoromethyl compound (4) is an intermediate in the reaction between the sulphide (2) and *p*-xylene in glass, since the glass could function as a Lewis acid both towards the Claisen intermediate (24) as well as towards compound (4) in the formation of the *p*-xylene derivative (8).

Experimental

¹H (60 MHz) and ¹⁹F N.m.r. (56.4 MHz) spectra were obtained with a Varian 360L spectrometer. Chemical shifts are upfield from internal CFCl₃ (δ_F), or downfield from internal SiMe₄ (δ_H).

Synthesis of Pentafluorophenyl Prop-2-ynyl Sulphide (1).—Pentafluorothiophenol (50.0 g) and dry tetrahydrofuran (400 ml) were cooled to -70 °C under nitrogen and *n*-butyl-lithium solution (1.6M; 156 ml) was added over a period of 2 h, the temperature being maintained at -70 °C. The last traces of *n*-butyl-lithium were washed into the reaction mixture with further dry tetrahydrofuran (50 ml). Prop-2-ynyl bromide [80% (w/w) in toluene; 37 g] was then added over 50 min at -70 °C. The mixture was allowed to warm to room temperature over 3 h, diluted with water (800 ml), acidified with hydrochloric acid (11M; 50 ml) and extracted with diethyl ether (2 × 300 ml). Some unchanged pentafluorothiophenol present in the reaction mixture was removed by shaking with sodium carbonate (1M; 100 ml). The organic extracts were dried (MgSO₄), the solvents evaporated, and the product distilled under reduced pressure to give pentafluorophenyl prop-2-ynyl sulphide (1) (42.21 g, 71%), b.p. 93 °C at 18 mmHg (Found: C, 45.1; H, 1.0. C₉H₃F₅S

requires C, 45.4; H, 1.3%); $\delta_{\text{F}}(\text{CDCl}_3)$ 133.8, 153.8, and 163.2, in the ratio 2:1:2 respectively; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.25 (t, C \equiv CH) and 3.73 (d, CH₂).

Synthesis of 1,3,4,5,6,7,8-Heptafluoro-2-naphthyl Prop-2-ynyl Sulphide (2).—Octafluoronaphthalene (2.87 g) in dimethylformamide (5 ml) was added over 5 min to a stirred solution of freshly prepared sodium hydrosulphide (1.23 g) in dimethylformamide (15 ml) and ethylene glycol (5 ml) maintained at -55°C . The mixture was warmed to 15°C over 3 h, and prop-2-ynyl bromide [80% (w/w) in toluene; 1.63 g] was then added. The mixture was stirred at room temperature for 16 h, diluted with water, acidified (5M-HCl), and extracted with ether. The organic phase was dried (MgSO₄) the solvent evaporated, and the residue sublimed at $70^\circ\text{C}/0.05$ mmHg to give the crude product (2.19 g, 64%); recrystallisation of this material from light petroleum (b.p. 40 – 60°C) gave pure 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-ynyl sulphide (2), m.p. 63.5 – 64.5°C (Found: C, 48.45; H, 0.9. C₁₃H₃F₇S requires C, 48.15; H, 0.93%); $\delta_{\text{F}}(\text{CDCl}_3)$ 109.9 (dd, *peri* J_{F,F} 69 Hz), 130.5 (br d), 144.0 (dt, *peri* J_{F,F} 69 Hz); 146.6 and 148.6 (AB, sets of triplets, *peri* J_{F,F} 56 Hz), 153.2 (t) and 155.7 (br m) in the ratio 1:1:1:1:1:1:1 respectively; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.15 (t, acetylenic CH) and 3.72 (d, CH₂).

Isomerisation of Pentafluorophenyl Prop-2-ynyl Sulphide (1) in CF₂ClCFCl₂.—The sulphide (1) (3.35 g) and dry CF₂-ClCFCl₂ (20 ml) were sealed in a nickel Carius tube (vol. 80 ml) and heated to 180°C for 91 h. The resulting brown oil was washed from the tube using diethyl ether, the solvents were distilled through a 60 cm Vigreux column and the residue was distilled under reduced pressure; one fraction (0.643 g) b.p. $80^\circ\text{C}/0.01$ mmHg, was collected. Analytical t.l.c. of the distillate on silica using light petroleum (b.p. 30 – 40°C) as the eluant showed two components, one of which was unchanged sulphide (1) and ¹⁹F n.m.r. spectroscopy indicated the presence of 4,5,6,7-tetrafluoro-2-fluoromethylbenzo[b]thiophene (3) (0.43 g, 13%) in the mixture. The distillate was separated by chromatography on silica (6 in \times 2.5 in) using light petroleum (b.p. 30 – 40°C) as the eluant. The slower component, a solid, was sublimed at $40^\circ\text{C}/0.05$ mmHg and recrystallised from light petroleum (b.p. 40 – 60°C) to give pure 4,5,6,7-tetrafluoro-2-fluoromethylbenzo[b]thiophene (3), m.p. 49.5 – 50°C (Found: C, 45.65; H, 0.9. C₉H₃F₅S requires C, 45.4; H, 1.3%); $\delta_{\text{F}}(\text{CDCl}_3)$ 141.4 (t), 144.5 (t), 159.1 (t), 160.0 (t), and 201.9 (t, CH₂F) in the ratio 1:1:1:1:1 respectively; J_{gemF,H} 48 Hz; $\delta_{\text{H}}(\text{CDCl}_3)$ 7.38 (3-H) and 5.56 (d, CH₂).

Isomerisations of 1,3,4,5,6,7,8-Heptafluoro-2-naphthyl Prop-2-ynyl Sulphide (2).—(a) In CF₂ClCFCl₂. The sulphide (2) (0.880 g) and dry CF₂ClCFCl₂ (20 ml) were sealed under nitrogen in a nickel Carius tube and heated at 160°C for 24 h. The orange reaction product was washed from the tube using freshly distilled acetone, the solvents were evaporated and the residue was fractionally sublimed at 50 – $60^\circ\text{C}/0.005$ mmHg. The sublimate (0.365 g, 41%) was recrystallised from light petroleum (b.p. 80 – 100°C) to give pure 4,5,6,7,8,9-hexafluoro-2-fluoromethylnaphtho[2,1-b]thiophene (4) m.p. 78 – 79°C (Found: C, 48.4; H, 0.6. C₁₃H₃F₇S requires C, 48.2; H, 0.9%); $\delta_{\text{F}}(\text{CDCl}_3)$ 139.7 (d), 142.5 (t), 145.4 (dt, *peri* J_{7F,8F} 66 Hz), 149.7 (dd, *peri*-F), 156.7 (m) and 198.1 (t) in the ratio 1:1:1:1:2:1 respectively; $\delta_{\text{H}}(\text{CDCl}_3)$ 5.75 (d, CH₂F; J_{gemF,H} 49 Hz) and 8.2 (m) with intensities in the ratio 2:1 respectively.

(b) Vapour phase pyrolysis. The sulphide (2) (0.215 g) was distilled through a silica tube [60 cm \times 1.5 cm diam. packed with silica fibre, (20 cm \times 1.5 cm diam.)] heated at 360°C , into a trap cooled with liquid air connected to a high vacuum system (0.005 mmHg). The crude product was sublimed at 50 – $60^\circ\text{C}/$

0.005 mmHg to give the 2-fluoromethyl compound (4) (0.174 g, 81%).

Thermolyses of Pentafluorophenyl Prop-2-ynyl Sulphide (1) with Aromatic Hydrocarbons.—(a) With benzene. The sulphide (1) (2.0 g) and dry benzene (10 ml) were sealed in a nickel Carius tube and heated at 180°C for 96 h. The reaction product was washed from the tube with acetone, the solvents were evaporated and the crude residue was distilled at 0.005 mmHg with an external temperature of 200°C . The distillate (0.9 g) was shown by analytical t.l.c. analyses to be an extremely complex mixture (at least six components) and no attempt was made to isolate any individual component.

(b) With *p*-xylene. The sulphide (1) (2.0 g) and dry *p*-xylene (10 ml) were sealed in a nickel Carius tube, heated at 180°C for 96 h and worked-up as in (a). The crude product, a black oil, which was shown to contain four components by t.l.c. on silica [light petroleum (b.p. 40 – 60°) as eluant] was exhaustively distilled at 0.005 mmHg using an oil bath maintained at 190°C . The distillate (0.54 g) was analysed by ¹⁹F n.m.r. spectroscopy and it was estimated that 2-(2,5-dimethylbenzyl)-4,5,6,7-tetrafluorobenzo[b]thiophene (5) was present to the extent of 35% by weight, representing an overall yield of (0.189 g, 7%).

From a number of identical experiments, a combination of distillation, flash chromatography on silica [using light petroleum b.p. (40 – 60°C) as the eluant], sublimation and crystallisation from light petroleum b.p. (40 – 60°C) gave pure 2-(2,5-dimethylbenzyl)-4,5,6,7-tetrafluorobenzo[b]thiophene (5), m.p. 83.5 – 84°C (Found: C, 63.3; H, 4.0. C₁₇H₁₂F₄S requires C, 63.0; H, 3.7%); $\delta_{\text{F}}(\text{CDCl}_3)$ 142.4 (t), 146.0 (t), 161.4 (t), and 162.2 (t), in the ratio 1:1:1:1; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.25 (Me), 4.127 (CH₂), and 7.02 (overlapping 3-H and ArH).

Reactions of 4,5,6,7-Tetrafluoro-2-fluoromethylbenzo[b]thiophene (3) with Aromatic Hydrocarbons in Boron Trifluoride-Diethyl Ether.—(a) With benzene. A solution of the 2-fluoromethyl compound (3) (0.056 g), anhydrous diethyl ether (1 ml), dry benzene (1 ml), and boron trifluoride-diethyl ether (0.5 ml) were stirred at room temperature for 150 min. The mixture was diluted with water, extracted with ether, and the combined extracts were dried (MgSO₄). The solvents were evaporated and the residue, a single component by analytical t.l.c. on silica using light petroleum (b.p. 40 – 60°C) as the solvent, was sublimed at $70^\circ\text{C}/0.005$ mmHg to give 2-benzyl-4,5,6,7-tetrafluorobenzo[b]thiophene (6) (0.065 g, 93%), m.p. 91.5 – 92°C (Found: C, 60.8; H, 2.5. C₁₅H₈F₄S requires C, 60.8; H, 2.7%); $\delta_{\text{F}}(\text{CDCl}_3)$ 142.77 (t), 146.4 (t), 161.7 (t), and 162.4 (t) in the ratio 1:1:1:1; $\delta_{\text{H}}(\text{CDCl}_3)$ 4.19 (s, CH₂), 7.09 (3-H), and 7.30 (s, ArH).

(b) With *p*-xylene. A solution of the fluoromethyl compound (3) (0.07 g), anhydrous ether (1 ml), dry *p*-xylene (1 ml), and boron trifluoride-diethyl ether (0.5 ml) was stirred at 25°C for 150 min and worked-up as in (a) to give compound (5) (0.090 g) (94%).

Reaction of 1,3,4,5,6,7,8-Heptafluoro-2-naphthyl Prop-2-ynyl Sulphide (2) with Aromatic Hydrocarbons in a Nickel Tube.—(a) With benzene. The sulphide (2) (0.452 g) and dry benzene (10 ml) were sealed in a nickel Carius tube and heated to 160°C for 25 h. The mixture was worked up as before, and sublimation of the crude product at 60 – $100^\circ\text{C}/0.005$ mmHg, followed by flash chromatography of the sublimate using CCl₄/CHCl₃ (70:30, v/v) gave pure 2-benzyl-4,5,6,7,8,9-hexafluoronaphtho[2,1-b]thiophene (7) (0.083 g, 16%), m.p. 95 – 96°C [from light petroleum (b.p. 60 – 80°C)] (Found: C, 59.4; H, 2.0. C₁₅H₈F₆S requires C, 59.7; H, 2.1%); $\delta_{\text{F}}(\text{CDCl}_3)$ 140.9(d), 143.6 (t), 146.8 (dm, *peri*-J_{7F,8F} 64 Hz), 152.7 (dd, *peri*-F) and 158.4 (br d) in the

ratio 1:1:1:1:2 respectively; $\delta_{\text{H}}(\text{CDCl}_3)$ 4.3 (s, CH_2), 7.3 (s, ArH) and 7.8 (m, 3-H).

(b) *With p-xylene.* The sulphide (**2**) (0.855 g) and dry *p*-xylene (10 ml) were sealed in a nickel Carius tube, heated at 160 °C for 24 h and worked up as in (a). The major product (0.557 g, 51%) was crystallised from light petroleum (b.p. 80–100 °C) to give 2-(2,5-dimethylbenzyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-*b*]thiophene (**8**), m.p. 110–111 °C (Found: C, 61.2; H, 3.3. $\text{C}_{21}\text{H}_{12}\text{F}_6\text{S}$ requires C, 61.5; H, 3.0%; $\delta_{\text{F}}(\text{CDCl}_3)$ 139.6 (d), 142.0 (t), 145.9 (dm, *peri*- $J_{\text{F},8\text{F}}$ 64 Hz), 152.3 (dd, *peri*-F), and 157.7 (br d) in the ratio 1:1:1:1:2 respectively; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.28 (Me) 2.31 (Me), 4.25 (s, CH_2), 7.03 (m, ArH), and 7.70 (3-H).

*Reaction of 4,5,6,7,8,9-Hexafluoro-2-fluoromethylnaphtho[2,1-*b*]thiophene (4) with Aromatic Hydrocarbons in Boron Trifluoride-Diethyl Ether.*—(a) *With benzene.* The 2-fluoromethyl derivative (**4**) (0.116 g), dry benzene (1 ml), and boron trifluoride-diethyl ether (1 ml) were stirred at room temperature for 15 min, and worked-up to give compound (**7**) (0.122 g, 89%).

(b) *With p-xylene.* The fluoromethyl compound (**4**) (0.117 g), dry *p*-xylene (2 ml), and boron trifluoride-diethyl ether (1 ml) were stirred for 15 min at 25 °C and worked-up to give compound (**8**) (0.129 g, 87%).

A Semi-kinetics Study of the Reaction Between 1,3,4,5,6,7,8-Heptafluoro-2-naphthyl Prop-2-ynyl Sulphide (2) and p-Xylene at 160 °C in a Nickel Tube.—The sulphide (**2**) (0.185 g) and dry *p*-xylene (20 ml), were sealed in a nickel Carius tube, heated at 160 °C for 6 h and the mixture was worked-up. The integrated ^1H and ^{19}F n.m.r. spectra of the crude product showed the presence of compounds (**4**) and (**8**) in the ratio 75:25 respectively. Fractional sublimation gave (**4**) (0.118 g, 64%) and (**8**) (0.05 g, 21%). Similar experiments were carried out over different times; over 12 h the ratio of (**4**) to (**8**) was 61:39; over 18 h it was 47:53; and over 24 h it was 0:100, and (**8**) was isolated in 50% yield.

Thermolyses of 1,3,4,5,6,7,8-Heptafluoro-2-naphthyl Prop-2-ynyl sulphide (2) with p-Xylene at 140 °C.—(a) *In a nickel tube.* The sulphide (**2**) (0.265 g) and dry *p*-xylene (20 ml) were sealed in a nickel Carius tube, heated at 140 °C for 24 h and worked up as before to give compound (**4**) (0.163, 61%) and compound (**8**) the yield of which was estimated as 4% by using compound (**11**) as an internal standard.

(b) *In glass apparatus.* The sulphide (**2**) (0.573 g) and dry *p*-xylene (30 ml) were heated under reflux at 140 °C for 24 h and worked up as before. The product consisted of unchanged starting material (0.089 g, 15%) and compound (**8**) (0.62 g, 85%); no 2-fluoromethyl compound (**4**) could be detected by ^{19}F n.m.r.

Thermolyses of 1,3,4,5,6,7,8-Heptafluoro-2-naphthyl Prop-2-ynyl Ether (9) with p-Xylene at 140 °C.—(a) *In glass apparatus.* The ether (**9**) (0.257 g) and dry *p*-xylene (20 ml) were heated together under reflux at 140 °C in a glass reaction vessel for 20 h and worked up as before. Examination of the sublimed crude product by ^{19}F and ^1H n.m.r. failed to reveal the presence of any fluoromethyl compound (**11**); only one product was present, identified by i.r. spectroscopy as 2-(2,5-dimethylbenzyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-*b*]furan (**10**) (0.205 g, 62%).

(b) *In a nickel tube.* The ether (**9**) (0.284 g) and dry *p*-xylene (20 ml) were sealed in a nickel Carius tube, heated at 140 °C for 20 h, and worked-up as in (a). ^1H n.m.r. analysis of the sublimate (0.157 g) showed the presence of (**11**) and (**10**) in the ratio of 90:10 respectively (yields of 48 and 5% respectively).

*Reaction of 4,5,6,7,8,9-Hexafluoro-2-fluoromethylnaphtho[2,1-*b*]furan (11) with p-Xylene at 140 °C in Glass Apparatus.*—

The fluoromethyl derivative (**11**) (0.281 g) and dry *p*-xylene (20 ml) were heated under reflux in a glass reaction vessel for 20 h at 140 °C, and worked up as before. ^{19}F and ^1H n.m.r. spectroscopy showed that no unchanged starting material was present in the crude product, which upon crystallisation from ethanol gave compound (**10**) (0.280 g, 78%).

*Reaction of 4,5,6,7,8,9-Hexafluoro-2-fluoromethylnaphtho[2,1-*b*]furan (11) with p-Xylene in Boron Trifluoride-Diethyl Ether.*—A solution of the furan (**11**) (0.071 g), diethyl ether (1 ml), dry *p*-xylene (1 ml), and boron trifluoride-diethyl ether (0.5 ml) were stirred at room temperature for 150 min and worked-up to give compound (**10**) (0.089 g, 98%).

Reaction of 1,3,4,5,6,7,8-Heptafluoro-1,2-dihydro-1-propa-1,2-dienylnaphthalen-2-one (13) with p-Xylene in Boron Trifluoride-Diethyl Ether.—The allene (**13**) (0.029 g), dry *p*-xylene (1 ml) and boron trifluoride-diethyl ether (0.5 ml) were maintained at 25 °C for 2.5 h and 100 °C for 5 h but gave only unchanged starting material (by n.m.r. spectroscopy). When the mixture was heated under reflux at 120 °C with an external bath temperature of 140 °C for 3 h and worked-up as before, ^1H n.m.r. showed the ratio of (**10**) to unchanged (**13**) was 15:85 respectively.

Thermolyses of 1,3,4,5,6,7,8-Heptafluoro-2-naphthyl Prop-2-ynyl Ether (9) with Isopropylbenzene at 143 °C.—(a) *In glass apparatus.* The ether (**9**) (0.546 g) and dry isopropylbenzene (10 ml) were sealed *in vacuo* in a glass Carius tube, heated at 143 °C for 24 h, and the mixture was worked-up as before. The crude product examined by ^1H and ^{19}F n.m.r. spectroscopy showed no 2-fluoromethyl compound (**11**), and consisted of the mixture of isopropylbenzenes (**14**) and the naphthalenone (**13**) in the ratio of 94:6 respectively.

(b) *In a nickel tube.* The ether (**9**) (0.56 g) and isopropylbenzene (10 ml) were sealed in a nickel Carius tube, heated at 143 °C for 24 h to give compound (**11**) (0.366 g, 65%), and a mixture (0.086 g) which contained the isopropylbenzene derivatives (**14**) and the ether compound (**15**) in the ratio of 20:80 respectively (by ^1H n.m.r. spectroscopy) (yields of 2 and 14% respectively).

Thermolysis of 1,3,4,5,6,7,8-Heptafluoro-2-naphthyl Prop-2-ynyl Ether (9) with N,N-Diethylaniline in a Glass Carius Tube.—The ether (**9**) (0.608 g) and freshly distilled *N,N*-diethylaniline (10 ml) were sealed *in vacuo* in a glass Carius tube, heated to 140 °C for 24 h and worked up as previously described⁵ to give 4,5,6,7,8,9-hexafluoro-2-methylnaphtho[2,1-*b*]furan (**17**) (0.0056 g, 1%), the 2-fluoromethyl compound (**11**) (0.0138 g, 2%), 2-(*x*-diethylaminobenzyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-*b*]furan (0.017 g, 2%), and 2-(4-diethylaminobenzyl)-4,5,6,7,8,9-hexafluoronaphtho[2,1-*b*]furan (0.178 g, 21%).

*Attempted Reactions of 4,5,6,7,8,9-Hexafluoro-2-fluoromethylnaphtho[2,1-*b*]furan (11).*—(a) *With N,N-diethylaniline in glass.* The 2-fluoromethyl compound (**11**) (0.504 g) and freshly distilled *N,N*-diethylaniline (10 ml) were sealed *in vacuo* in a glass Carius tube, heated at 140 °C for 24 h and worked-up as previously to give unchanged 2-fluoromethyl compound (**11**) (0.490 g, 97%); no nitrogen-containing compounds (**16**) could be detected by ^{19}F n.m.r.

(b) *With p-xylene containing N,N-diethylaniline in glass.** Compound (**11**) (0.507 g), *p*-xylene (10 ml) and freshly distilled *N,N*-diethylaniline (5 ml) heated together exactly as in (a) gave unchanged (**11**) (0.497 g, 98%).

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