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PARTIALLY FLUORINATED HETEROCYCLIC COMPOUNDS. PART 23 [1]. THERMOLYSIS REACTIONS OF 1,3,4,5,6,7,8-HEPTAFLUORO-2-NAPHTHYL PROP-2-ENYL SULPHIDE AND 1,3,4,5,7,8-HEXAFLUORO-2,6-DI(PROP-2-ENYLTHIO)NAPHTHALENE IN NN-DIETHYLANILINE AND RELATED REACTIONS WITH 1,3,4,5,6,7,8-HEPTAFLUORO-1-(PROP-2-ENYL)-NAPHTHALEN-2-ONE AND 2,3,4,5,6-PENTAFLUORO-4-(PROP-2-ENYL)2,5-CYCLOHEXADIENONE

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SUMMARY

1,3,4,5,6,7,8-Heptafluoro-2-naphthyl prop-2-enyl sulphide (6) and 1,3,4,5,7,8-hexafluoro-2,6-di(prop-2-enylthio)naphthalene (7) were synthesised from octafluoronaphthalene. Compound (6) on heating with NN-diethylaniline (DEA) under reflux gave 4,5,6,7,8,9-hexafluoro-2,3-dihydro-2-methylnaphtho[2,1-b]thiophen (8) and a small amount of 5,6,7,8,9,10-hexafluoro-3,4-dihydro-2H-naphtho[2,1-b]thiopyran (9); under the same conditions compound (7) gave 4,5,9,10-tetrafluoro-2,3,7,8-tetrahydro-2,7-dimethylnaphtho[2,1-b:6,5-b']dithiophen (10) and a small amount of 4,5,10,11-tetrafluoro-2,3,8,9-tetrahydro-2-methyl-7H-thieno[3',2':5,6]naphtho[2,1-b]-thiopyran (11). 1,3,4,5,6,7,8-Heptafluoro-1-(prop-2-enyl)naphthalen-2-one (4) in refluxing DEA gave 3,4,5,6,7,8-hexafluoro-1-(prop-2-enyl)-2-naphthol (13) and 4,5,6,7,8,9-hexafluoro-2,3-dihydro-2-methylnaphtho[2,1-b]furan (12); (13) is an intermediate in the formation of (12) from (4). 2,3,4,5,6-Pentafluoro-4-(prop-2-enyl)-2,5-cyclohexadienone (5) in refluxing DEA gave 2,3,5,6-tetrafluoro-4-(prop-2-enyl)phenol (14). The solvent DEA forms blood-red solutions with (4) and (5) indicative of an electron transfer process; it is proposed that the solvent causes the reduction of the carbonyl or thiocarbonyl group in the Claisen rearrangement products, followed by dehydrofluorination prior to cyclisation reactions taking place.

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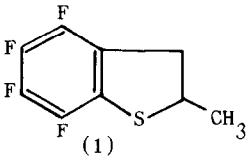
INTRODUCTION

In an earlier paper in this series [2] pentafluorophenyl prop-2-enyl sulphide in refluxing NN-diethylaniline was shown to give a complex mixture of at least fourteen products, two of those isolated, 4,5,6,7-tetrafluoro-2,3-dihydro-2-methylbenzo[b]thiophen (1) (5%) and 5,6,7,8-tetrafluoro-3,4-dihydro-2H-benzo[b]-thiopyran (2) (2%) being accounted for on the basis of a Claisen rearrangement intermediate (3). Recently the preparation of 1,3,4,-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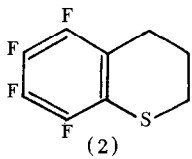
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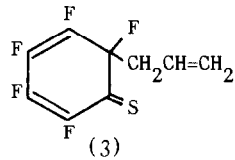
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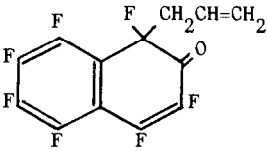
5,6,7,8-heptafluoro-2-naphthyl prop-2-ynyl sulphide was reported from our laboratory [3], and it was of interest to prepare the corresponding 2-naphthyl prop-2-enyl sulphide and examine its reaction in NN-diethylaniline. We also report in this paper the thermolysis reactions of 1,3,4,5,6,7,8-heptafluoro-1-(prop-2-enyl)naphthalen-2-one (4) [4] and 2,3,4,5,6-penta-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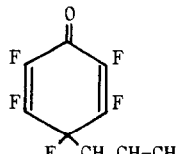
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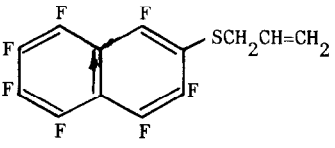
fluoro-4-(prop-2-enyl)-2,5-cyclohexadienone (5) [5] in NN-diethylaniline.

RESULTS AND DISCUSSION

The addition of octafluoronaphthalene to sodium hydrosulphide in a mixture of ethylene glycol and dimethylformamide at -6° followed by prop-2-enyl bromide gave 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-enyl sulphide (6) (36%) and 1,3,4,5,7,8-hexafluoro-2,6-di(prop-2-enylthio)naphthalene (7) (31%) (peri J_{F-F} 70 Hz).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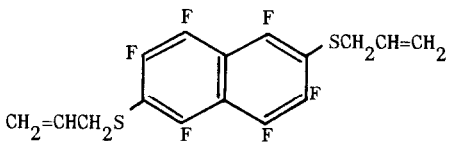
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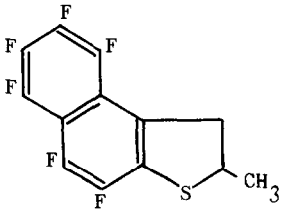
When the sulphide (6) was heated in NN-diethylaniline under reflux for 10 h, the crude product (83%) was shown to consist principally of 4,5,6,7,8,-9-hexafluoro-2,3-dihydro-2-methylnaphtho[2,1-b]thiophen (8) (93 parts) and 5,6,7,8,9,10-hexafluoro-3,4-dihydro-2H-naphtho[2,1-b]thiopyran (9) (7 parts). Compound (8) was isolated pure and its ^{19}F nmr spectrum showed only one large peri J_{F-F} coupling constant (61 Hz) which indicated the loss of the



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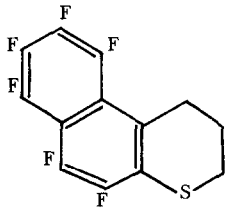
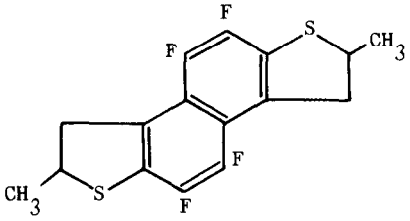


(9)

fluorine at C-1 from the starting material (6). The minor component (9) could not be isolated, but the presence of the 3,4-dihydro-2H-thiopyran ring structure was evident from the ^{1}H nmr spectrum of the crude product when compared with that of (2) [2]. The di(prop-2-enylthio) compound (7) also gave two isomeric cyclised products (79%) in the ratio 90:10 when heated under reflux for 10 h in NN-diethylaniline. The major component of the mixture, the dithiophen derivative (10) was obtained pure, but the minor component (11) could not be separated from (10).



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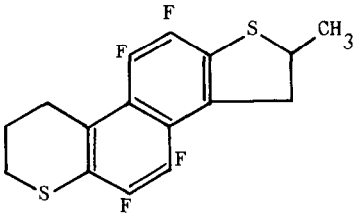
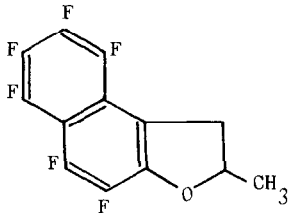


(11)

In previous experiments with prop-2-enyl ethers, only one liquid phase reaction has been reported: that involving 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-enyl ether in refluxing xylene which gave the Claisen rearrangement product (4) [4]. It was of interest therefore to test the use of refluxing NN-diethylaniline with (4). At room temperature these two materials gave a blood-red solution instantaneously, and after heating the solution under reflux for 20.5 h, the oxygen analogue of (8), compound (12) (33%) was isolated. When the same reaction was carried out for only 1 h, compound (12) was formed (7%), but the major product was 3,4,5,6,7,8-hexa-



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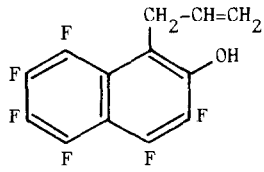

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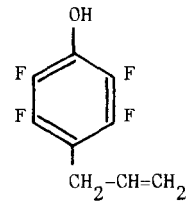
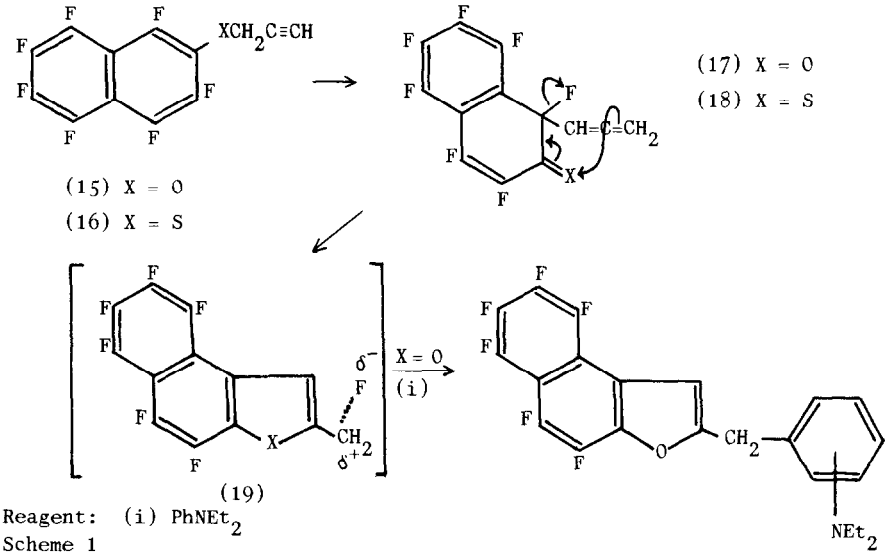


(14)

fluoro-1-(prop-2-enyl)-2-naphthol (13) (40%). In a separate experiment in refluxing NN-diethylaniline over 20.5 h, the naphthol (13) gave the cyclised product (12) (64%) with 22% of (13) being recovered, indicating the intermediacy of (13) in the conversion of the Claisen rearrangement compound (4) into (12). 2,3,4,5,6-Pentafluoro-4-(prop-2-enyl)-2,5-cyclohexadienone (5) [5] also formed a blood-red solution with NN-diethylaniline at room temperature, and on refluxing the mixture for 5 min. gave 2,3,5,6-tetrafluoro-4-(prop-2-enyl)phenol (14) (67%).

Recently it was established that the reactions of 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-ynyl ether (15) and sulphide (16) proceed via the heterolytic cleavage of the sp^3 C-F bond in the intermediate Claisen rearrangement products (17) and (18) to give the charge-separated species (19) which, with the oxygen compound, effects electrophilic replacement of hydrogen in the reactive solvent (Scheme 1) [3]. Significantly, in the



(15) X = O
(16) X = S

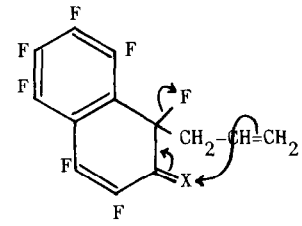
(17) X = O
(18) X = S

(19)

Reagent: (i) $PhNEt_2$

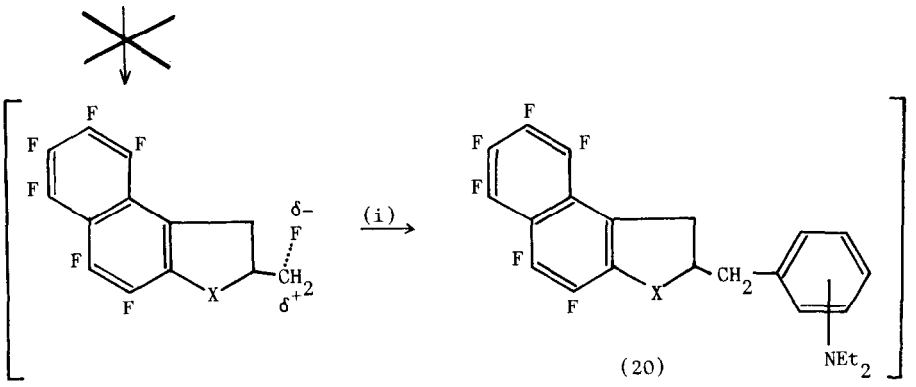
Scheme 1

work described in this paper, no products of the type (20) are formed, so that an ionic process analogous to that shown in Scheme 1 where allylic fluorine is displaced, is not operating (Scheme 2).



(4) X = O

(21) X = S

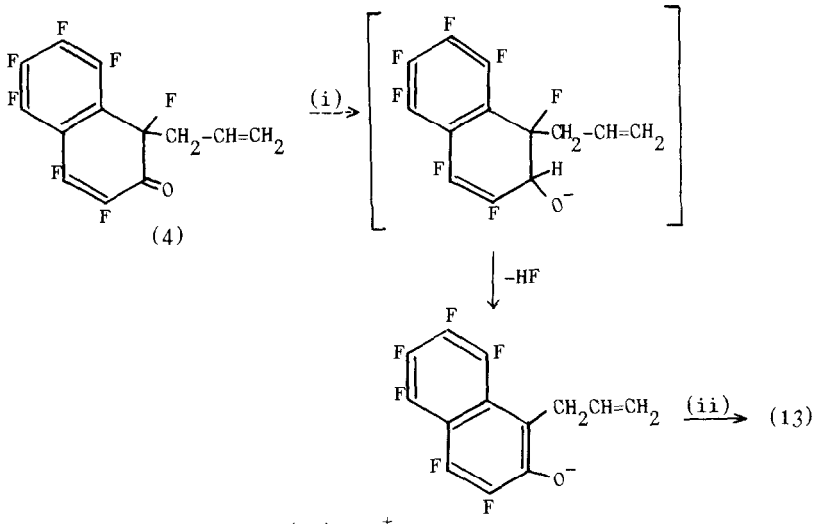


Reagent: (i) $PhNEt_2$

Scheme 2

The formation of the blood-red solutions from both the naphthalenone (4) and cyclohexadienone (5) with NN-diethylaniline is strongly indicative of an electron transfer process from the solvent. This suggests that the initial reaction involves overall reduction of the carbonyl group and loss of hydrogen fluoride with rearomatisation of the ring as illustrated for the naphthalen-2-one in Scheme 3 for the formation of the 2-naphthol derivative (13). A Markovnikov addition to the double bond in (13) initiated by protonation of the terminal carbon of the alkene accounts for the formation of the oxygen heterocycle (12).

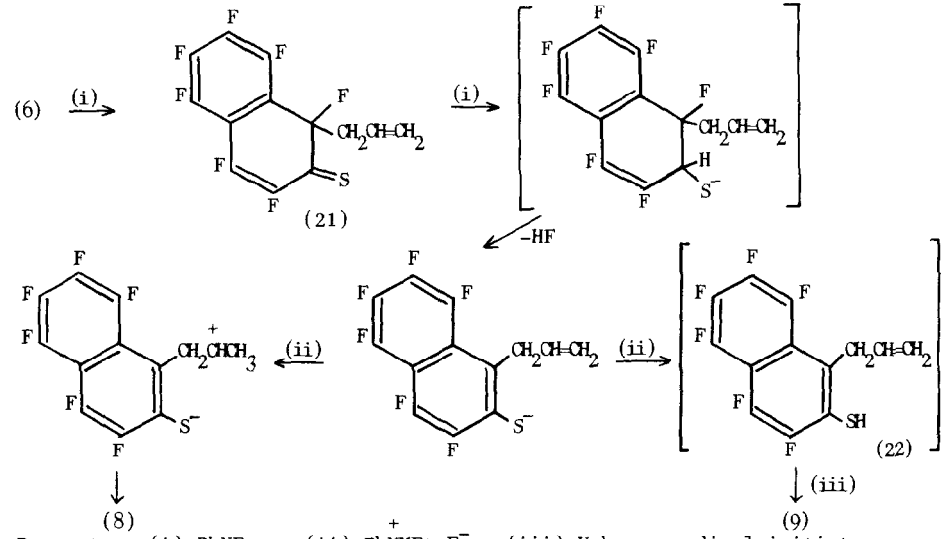
Although the initial Claisen rearrangement products from pentafluorophenyl prop-2-enyl sulphide, the 2-naphthyl sulphide (6) and the 2,6-di-(prop-2-enylthio) compound (7) have not been isolated, the experiments with



Reagent: (i) $PhNEt_2$; (ii) H_3O^+

Scheme 3

related oxygen compounds described in this paper strongly suggest that an analogous reduction of the thiocarbonyl group could be the major reaction taking place initially. The reaction sequences are illustrated in Scheme 4 with the 2-naphthyl sulphide (6). The formation of the small proportion of the 3,4-dihydro-2H-thiopyran derivative (9) requires the attack by a sulphur



Reagents: (i) $PhNEt_2$; (ii) $PhNHEt_2F^-$; (iii) Unknown radical initiator

Scheme 4

radical on the terminal carbon of the alkene followed by hydrogen atom abstraction. By analogy with the mechanism proposed in an earlier paper [2], the required radical species could arise via homolytic cleavage of the sp^3 C-F bond in the Claisen rearrangement product (21), or via some unknown initiating species on the 2-thiol (22).

Finally, it is interesting to note that with the naphthalen-2-one (4), no evidence was found for the formation of 5,6,7,8,9,10-hexafluoro-2H-naphtho[2,1-b]pyran which could have arisen by an initial dehydrofluorination of (4) with the basic solvent [6].

EXPERIMENTAL

^1H (60 MHz) and ^{19}F (56.4 MHz) nmr spectra were obtained with a Varian EM360L spectrometer, A; ^1H (250 MHz) and ^{19}F (235.34 MHz) nmr spectra were obtained on a Brüker AC250 spectrometer, B; and ^1H (300.13 MHz) nmr spectra were obtained on a Brüker WM300WB spectrometer, C, located in the Chemistry Department, University of Newcastle. Chemical shifts are downfield from internal $SiMe_4$ (δ_H) (on instrument A, B or C) or upfield from internal $CFCl_3$ (δ_F) (on instrument A or B).

Reaction of octafluoronaphthalene with sodium hydrosulphide

Octafluoronaphthalene (10.0 g) in dimethylformamide (25 ml) was added over 45 min. to a stirred solution of sodium hydrosulphide (4.34 g) in dimethylformamide (50 ml) and ethylene glycol (15 ml) maintained at -6°C. Prop-2-enyl bromide (4.5 g) in dimethylformamide (5 ml) was added to the mixture, and the reaction temperature was raised to and maintained at 50°C for 1 h. 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 ($MgSO_4$), the solvent evaporated and the residue separated by flash chromatography on silica (160 mm x 50 mm) using light petroleum (b.p. 40-60°) as eluant. Four fractions were collected and subjected to molecular distillation/sublimation at 0.05 mm Hg to give: (i) a yellow liquid (4.37 g) from 55-60°C; (ii) a yellow liquid (0.16 g) from 60-70°C; (iii) a yellow solid (0.57 g) from 70-100°C; and (iv) a yellow solid (3.58 g) from 100-140°C. Fraction (i) was mainly one component which was isolated by further chromatography and recrystallisation from light petroleum (b.p. 30-40°C) to give 1,3,4,5,6,7,8-heptafluoro-2-naphthyl prop-2-enyl sulphide (6) nc m.p. 33-34° (Found: C, 47.9; H, 1.1. $C_{13}H_5F_7S$ requires C, 47.85;

H, 1.55%); δ_F ($CDCl_3$) (A) 108.9 (dd, peri J_{F-F} 71 Hz), 128.7 (brd), 143.0 (dt, peri J_{F-F} 71 Hz), 145.5 and 147.6 (AB sets of triplets, peri J_{F-F} 58 Hz), 152.5 (t) and 154.7 ppm (t) in the ratio 1:1:1:1:1:1.

Fractions (ii), (iii) and (iv) (mainly one component) were combined and recrystallised from light petroleum (b.p. 80-100°) to give 1,3,4,5,7,8-hexafluoro-2,6-di(prop-2-enylthio)naphthalene (7) nc m.p. 82-83° (Found: C, 50.6; H, 2.3. $C_{16}H_{10}F_6S_2$ requires C, 50.50; H, 2.65%); δ_F ($CDCl_3$) (A) 111.6 (dd, peri J_{F-F} 70 Hz), 132.4 (d) and 148.1 ppm (dt, peri J_{F-F} 70 Hz) in the ratio 1:1:1. The yields of (6) and (7) were 36% and 31% respectively.

Reactions in NN-diethylaniline

(a) 1,3,4,5,6,7-Heptafluoro-2-naphthyl prop-2-enyl sulphide (6)

The sulphide (6) (0.515 g) and freshly distilled NN-diethylaniline (10 ml) were heated under reflux for 10 h and the mixture was worked-up by dissolving in ether and washing with sulphuric acid to remove nitrogen-containing materials. The ether was dried ($MgSO_4$), the solvent evaporated and the residue sublimed at 50-86°/0.05 mm. The sublimate (0.404 g, 83%) was examined by ^1H nmr spectroscopy (B) and shown to contain mainly two components (8) and (9) in the ratio of 93:7. The major component was separated by a combination of flash chromatography on silica using light petroleum (b.p. 40-60°) and recrystallisation from the same solvent to give 4,5,6,7,8,9-hexafluoro-2,3-dihydro-2-methylnaphtho[2,1-b]thiophen (8) nc, m.p. 89.5-90° (Found: C, 50.9; H, 1.7; M^+, 308. $C_{13}H_6F_6S$ requires C, 50.65; H, 1.95%; M, 308); δ_F (C_6H_6) (B) 137.0 (t), 145.4 (t), 146.6 (overlapping AB, peri J_{F-F} 61 Hz), 158.5 (t) and 159.6 ppm (t) in the ratio 1:1:2:1:1; δ_H ($CDCl_3$) (C) 1.55 (d, CH_3), 3.55 and 3.97 (AB set of doublets, J_{H-H} 17.5 Hz, $-CH_2-$) and 4.25 (m, $-CH-$).

The minor component could not be separated from the mixture but was identified as 5,6,7,8,9,10-hexafluoro-3,4-dihydro-2H-naphtho[2,1-b]thiopyran (9) by its ^1H nmr spectrum: δ_H ($CDCl_3$) (C) 2.25, 3.05 and 3.33 in the ratio 1:1:1.

The aqueous acid solution containing soluble nitrogen compounds from the original work-up was treated with excess sodium hydroxide, extracted with ether and the dried ($MgSO_4$) extracts distilled to remove ether. Further distillation in vacuo at $\leq$ 40°/0.05 mm removed NN-diethylaniline, and examination of the tarry residue (0.0923 g) by ^{19}F nmr (B) showed that only minute amounts of fluorine-containing material were present.

(b) 1,3,4,5,7,8-Hexafluoro-2,6-di(prop-2-enylthio)naphthalene (7)

Compound (7) (0.504 g) and NN-diethylaniline (10 ml) were heated under reflux for 10 h and the mixture was worked-up as in (a). The crude product, shown by ^{1}H nmr spectroscopy (B) to contain two major components (10) and (11) in the ratio 90:10, was freed from minor products by flash chromatography on silica using $CCl_4/CHCl_3$ (70/30 v/v). This material (0.363 g, 79%) was enriched in the major component by further chromatography on silica using CCl_4, and extensive fractional crystallisation from light petroleum (b.p. 100-120°) gave 4,5,9,10-tetrafluoro-2,3,7,8-tetrahydro-2,7-dimethylnaphtho[2,1-b:6,5-b']dithiophen (10) nc m.p. 195-195.5° (Found: C, 56.1; H, 3.7; M^+, 344. $C_{16}H_{12}F_4S_2$ requires C, 55.80; H, 3.50%; M, 344); δ_F ($CDCl_3$) (B) 139.6 (d) and 145.6 ppm (d), J_{F-F} 21 Hz, in the ratio 1:1; δ_H ($CDCl_3$) (C) 1.53 (d, CH_3), 3.54 and 3.95 (AB sets of doublets, J_{H-H} 17.5 Hz, CH_2) and 4.21 (m, -CH).

The minor component could not be separated from the mixture but was identified as 4,5,10,11-tetrafluoro-2,3,8,9-tetrahydro-2-methyl-7H-thieno-[3',2':5,6]naphtho[2,1-b]thiopyran (11) by its ^{1}H and ^{19}F nmr spectra: δ_H ($CDCl_3$) (C) 2.23, 3.05 and 3.35 in the ratio 1:1:1; δ_F ($CDCl_3$) (B) 139.1, 140.3, 141.1 and 146.9 ppm.

The aqueous phase from the original work-up was examined for nitrogen-containing fluorine compounds as in (a) using ^{19}F nmr (B). The tar (0.136 g) contained only minute amounts of fluorine-containing material.

(c) 1,3,4,5,6,7,8-Heptafluoro-1-(prop-2-enyl)naphthalen-2-one (4)

(i) Compound (4) (0.500 g) and NN-diethylaniline (10 ml) immediately turned blood-red on mixing. The mixture was heated under reflux for 20.5 h and worked-up as in (a). The crude product shown by thin layer chromatography to contain one major component, was subjected to flash chromatography on silica (160 mm x 50 mm) using $CCl_4/CHCl_3$ (9:1 v/v) and then sublimed at 80°/0.05 mm Hg. The sublimate (0.154 g, 33%) was recrystallised from light petroleum (b.p. 40-60°) to give 4,5,6,7,8,9-hexafluoro-2,3-dihydro-2-methyl-naphtho[2,1-b]furan (12) nc, m.p. 86.5-87° (Found: C, 53.3; H, 1.7; M^+, 292. $C_{13}H_6F_6O$ requires C, 53.45; H, 2.05%; M, 292); δ_F ($CDCl_3$) (B) 144.6 (dd, peri J_{F-F} 59 Hz), 147.0 (dt, peri J_{F-F} 59 Hz), 149.7 (t), 158.0 (overlapping m) and 161.4 ppm (t) in the ratio 1:1:1:2:1; δ_H ($CDCl_3$) (C) 1.60 (d, CH_3), 3.31 and 3.83 (AB sets of doublets CH_2, J_{H-H} 15 Hz) and 5.30 (m, -C-H).

The aqueous phase from the original work-up was examined for nitrogen-containing fluorine compounds as in (a) using ^{19}F nmr (B). The tar (0.165 g) contained no fluorine.

(ii) Compound (4) (0.516 g) and NN-diethylaniline (10 ml) were heated under reflux for 1 h and the product was worked up as in (a). Flash chromatography of the product on silica using $CCl_4/CHCl_3$ (9:1 v/v) gave the 2,3-dihydro-2-methyl furan derivative (12) (0.033 g; 7%) and a slower moving component (0.196 g; 40%) separated from other minor components by dissolving in sodium hydroxide, washing the solution repeatedly with ether, acidifying the solution and re-extracting the organic component with ether. Sublimation of this material at $70^{o}/0.05$ mm Hg and recrystallisation from light petroleum (b.p. 40-60°) gave 3,4,5,6,7,8-hexafluoro-1-(prop-2-enyl)-2-naphthol (13) nc m.p. 59-59.5° (Found: C, 53.5; H, 2.1; M^+, 292. $C_{13}H_6F_6O$ requires C, 53.45; H, 2.05%; M, 292); δ_F ($CDCl_3$) (B) 144.3 (t), 145.2 (dd, peri J_{F-F} 67 Hz), 147.2 (dt, peri J_{F-F} 67 Hz), 157.2 (bt), 158.0 (bd) and 160.1 ppm (t) in the ratio 1:1:1:1:1:1; δ_H ($CDCl_3$) (C) 3.92 (CH_2), 4.97 and 5.08 (CH_2=), 5.81 (OH) and 6.07 (=CH-); ν_{max} 3460 cm^{-1} (OH).

(d) 3,4,5,6,7,8-Hexafluoro-1-(prop-2-enyl)-2-naphthol (13)

The 2-naphthol (13) (0.085 g) and NN-diethylaniline (5 ml) were heated together under reflux for 20.5 h, the product was isolated as in (a) and its two components were separated by thick layer chromatography on silica (20 cm x 20 cm) using $CHCl_3/CCl_4$ (30:70 v/v) to give the 2,3-dihydro-2-methyl furan compound (12) (0.054 g, 64%) and unreacted starting material (13) (0.019 g, 22%).

(e) 2,3,4,5,6-Pentafluoro-4-(prop-2-enyl)-2,5-cyclohexadienone (5)

The dienone (5) (2.124 g) and NN-diethylaniline (10 ml) formed an immediate blood-red coloured solution on mixing. The mixture was heated under reflux for 5 min. and worked up as in (a). The residue was distilled at room temperature/0.05 mm to give crude product (1.311 g, 67%). Further purification by flash chromatography on silica/CH_2Cl_2, micro-distillation and recrystallisation from light petroleum (b.p. 30-40°) at low temperatures gave 2,3,5,6-tetrafluoro-4-(prop-2-enyl)phenol (14) nc m.p. 16-19° (Found: C, 52.5; H, 3.1. $C_9H_6F_4O$ requires C, 52.45; H, 2.95%); δ_F ($CDCl_3$) (B) 146.6 (dd) and 164.8 ppm (dd, J_{F-F} 22.5 Hz) in the ratio 1:1; δ_H ($CDCl_3$) (B) 3.33 (CH_2), 4.83 and 5.13 (CH_2=), 5.6 (OH) and multiplet between 5.5 and 6.2 (=CH-); ν_{max} 3565 cm^{-1} (free OH) and 3410 cm^{-1} (broad OH).

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