Reactions of Polyfluoro-arenols and -heteroarenols with Activated Dimethyl Sulphoxide. Facile [2,3]-Sigmatropic Rearrangement Reactions giving De-aromatised Products

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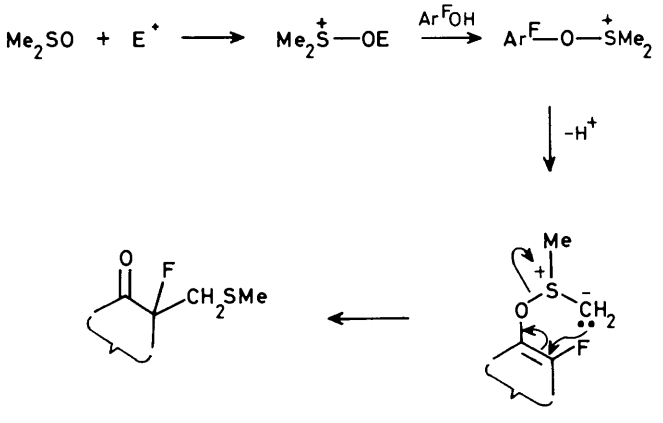
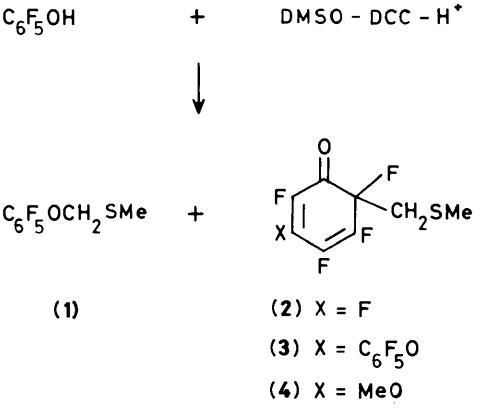
Pentafluorophenol reacted with the reagent dimethyl sulphoxide–dicyclohexylcarbodi-imide–ortho-phosphoric acid below room temperature to give the ether (**1**), the [2,3]-rearrangement product (**2**), and (**3**) a derivative of (**2**). Under similar conditions, 2,3,5,6-tetrafluorophenol gave (**7**) and (**8**), and 1,3,4,5,6,7,8-heptafluoro-2-naphthol gave (**12**) and (**13**). Reaction of polyfluoroarenols with dimethyl sulphoxide–trifluoroacetic anhydride at low temperatures followed by deprotonation with triethylamine resulted in more efficient rearrangement reactions; 4-bromo-3,5,6-trifluoropyridin-2-ol gave the ether (**14**) and the products of rearrangement both to carbon and nitrogen, (**15**) (after hydrolysis) and (**16**) respectively; 2,4,5,6-tetrafluoropyridin-3-ol resulted in the overall replacement of the 2-fluorine by CHO (**17**) and by $CH(SMe)_2$ (**18**); and with 2,5,6-trifluoropyrimidin-4-ol and 5-fluoro-4,6-dimethoxypyrimidine-2-ol, simple rearrangement products (**21**) and (**22**) were obtained. Hydrolysis of (**21**) gave the 5-fluorouracil derivative (**23**). Sodium borohydride reduction and Raney nickel desulphurisations of some of the rearrangement compounds gave phenolic products. Reaction of the sulphone from (**13**) with base (DBU) effected the overall efficient replacement of the 1-fluorine in the 2-naphthol by CHO (**35**) and by $CH(SO_2Me)_2$ (**36**).

In previous papers the thermolyses of some polyfluoroaryl [1] and -heteroaryl [2] prop-2-enyl ethers have been described and we have also reported related work with prop-2-enyl sulphides,[3] prop-2-ynyl ethers [4] and prop-2-ynyl sulphides.[5] A variety of products resulted from the presumed initial 3,3-sigmatropic (*i.e.* Claisen) rearrangement to an *ortho* carbon bearing a fluorine in each of these substrates, though with prop-2-enyl 2,5,6-trifluoropyrimidin-4-yl ether [6] only rearrangement to N-3 occurred. The re-aromatisation of all the initial rearrangement products is precluded structurally. We now report the first examples of 2,3-sigmatropic (*i.e.* Sommelet-Hauser) rearrangements in some polyfluoro-aromatic and -heteroaromatic systems in which an *ortho* carbon bearing a fluorine or an *ortho* nitrogen is the migration terminus.

The fundamental reaction that has been studied has involved polyfluoro-arenols and -heteroarenols with activated dimethyl sulphoxide and the attempted rearrangement of the intermediate ylide formed by deprotonation and is illustrated in Scheme 1 for a polyfluoroarenol Ar^F–OH. The pioneering work in this area was carried out by Pfitzner and Moffat [7] who treated a variety of phenols with dimethyl sulphoxide (DMSO), dicyclohexylcarbodi-imide (DCC), and anhydrous phosphoric acid (H^+) in dry benzene. The reaction of pentafluorophenol with DMSO–DCC–H^+ in benzene was exothermic, but by maintaining the temperature at or below 12 °C, three products were isolated: the ether (**1**) (6%), the cyclohexa-2,4-dienone (**2**) (13%), and (**3**) a pentafluorophenoxy substitution product of (**2**) (36%) (Scheme 2). All the fluorines in (**2**) have been assigned in



Scheme 1.



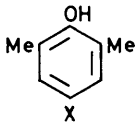
Scheme 2.

the ^{19}F n.m.r. spectrum and the absence of the lowest field absorption at *ca.* 132 p.p.m. (assigned to 3-F) in (**3**) indicated the site of replacement of fluorine in (**2**) by C_6F_5O. The ease of replacement of the fluorine at C-3 was demonstrated in a separate experiment by the addition of methanol to (**2**) at room temperature which gave the 3-methoxy compound (**4**). Other workers have noted the lability of fluorine at the same site in related cyclohexa-2,4-dienone compounds.[8]

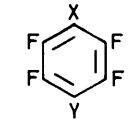
The formation of methylthiomethyl compounds had been observed in the earlier work. Of special interest is the reaction involving pentachlorophenol which gave 60% of the methylthiomethyl ether $C_6Cl_5OCH_2SMe$ and *no* 2,3-rearrangement products,[7b] in contrast to the work reported here. Dissociation

of the intermediate ylide into $C_6Cl_5O^-$ and $CH_2{=}\overset{+}{S}Me$ followed by recombination rationalised the formation of the ether.

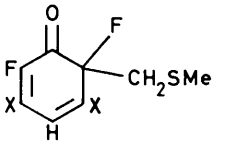
The presence of the species $Me\overset{+}{S}{=}CH_2$ in the reacting systems has been implicated in the formation of (**5**) from 2,6-dimethylphenol (**6**) under the prevailing acid conditions of the DMSO–DCC–H^+ reagent [7b,d] and it was of interest to test whether a related electrophilic substitution product would be obtained from 2,3,5,6-tetrafluorophenol under similar reaction



(**5**) X = CH_2SMe
(**6**) X = H



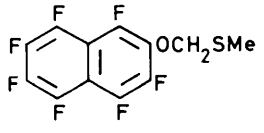
(**7**) X = OCH_2SMe, Y = H
(**9**) X = OH, Y = CH_2SMe
(**11**) X = OH, Y = CH_2OH



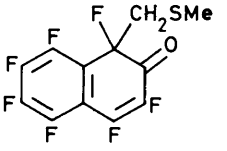
(**8**) X = F
(**10**) X = C_6F_5O

conditions. Two products were obtained: methylthiomethyl ether (**7**) (8%) and the cyclohexa-2,4-dienone (**8**) (69%). The 4-methylthiomethyl compound (**9**) was not formed, nor was any fluorine substitution product from (**8**), though in a separate experiment with pentafluorophenol and potassium carbonate in refluxing tetrahydrofuran the disubstituted compound (**10**) (66%) was obtained. When the cyclohexa-2,4-dienone (**8**) was treated at room temperature with liquid HF, three products were obtained: 2,3,5,6-tetrafluorophenol (19%); the 4-methylthiomethyl compound (**9**) (28%), thereby indicating the formation of the electrophile $Me\overset{+}{S}{=}CH_2$; and the methanol derivative (**11**) (14%), presumably derived from (**9**) by an acid-catalysed hydrolysis.

1,3,4,5,6,7,8,-Heptafluoro-2-naphthol and DMSO–DCC–H^+ gave the methylthiomethyl ether (**12**) (10%) and the 2,3-rearrangement compound (**13**) (72%). The structure of (**13**) was



(**12**)

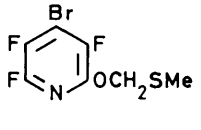


(**13**)

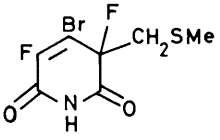
determined by ^{19}F n.m.r. spectroscopy which showed only one peri J_{F-F} (76 Hz) demonstrating C-1 rather than C-3 as the migration terminus.

A practical problem associated with the reagent DMSO–DCC–H^+ is the separation of the products from precipitated dicyclohexylurea. However a wide range of activated dimethyl sulphoxide reagents are now available [9] and we have found that DMSO–trifluoroacetic anhydride [10] (TFAA) in anhydrous methylene dichloride at −60 °C is very easy to use in reactions with polyfluoro-arenols and -heteroarenols. The addition of triethylamine (TEA) at −35 °C brings about formation of the ylide prior to the molecular rearrangement taking place. No methylthiomethyl ethers were formed at the low reaction temperature with either pentafluorophenol or 1,3,4,5,6,7,8-heptafluoro-2-naphthol. With the former compound, the cyclohexa-2,4-dienone (**2**) was obtained in 71% yield accompanied by (**3**) (17%) whereas the naphthol gave the rearranged compound (**13**) (78%) with 6% of starting material being recovered unchanged.

We have examined the low temperature reactions of some fluorine-containing pyridinols and pyrimidinols with the reagent DMSO–TFAA followed by treatment with TEA, an area which has not been investigated with hydrogen-containing analogues. Surprisingly, no reaction whatsoever occurred with the readily accessible 2,3,5,6-tetrafluoropyridine-4-ol.[11] With 4-bromo-2,3,5-trifluoropyridin-6-ol [12] however, not only was the methoxymethyl ether (**14**) isolated (1.5%), but both 2,3-rearrangements to carbon (followed by hydrolysis) and to nitrogen termini also occurred giving (**15**) (8%) and (**16**) (44%) respectively.



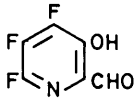
(**14**)



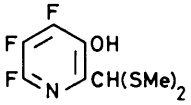
(**15**)

(**16**)

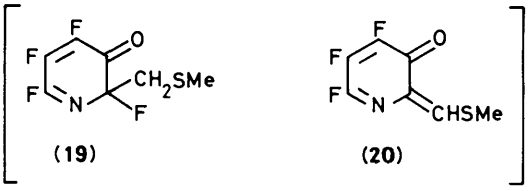
The reaction of 2,4,5,6-tetrafluoropyridin-3-ol [2] with DMSO–TFAA followed by treatment with TEA was complex, but two unexpected compounds were isolated in low yield: the hydroxy aldehyde (**17**) (6%) and its methyl thioacetal (**18**) (6%). The



(**17**)



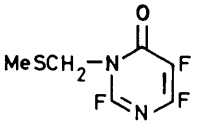
(**18**)



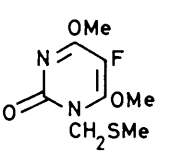
(**19**) (**20**)

formation of both of these compounds can be rationalised as arising from a common origin, the 2,3-rearrangement compound (**19**) which can lose HF to give (**20**). Addition of water to (**20**) with re-aromatisation and hydrolysis of the hemithioacetal would give (**17**), while the released MeS^- could attack (**20**) to give (**18**).

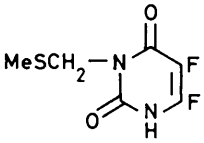
2,5,6-Trifluoropyrimidin-4-ol [13] reacted with DMSO–TFAA followed by treatment with TEA to give exclusively the 2,3-rearrangement to nitrogen, compound (**21**) (71%), the same terminus for the 3,3-sigmatropic rearrangement with the corresponding prop-2-enyl ether.[6] 5-Fluoro-4,6-dimethoxypyrimidin-2-ol under similar conditions gave (**22**) (59%), whereas the corresponding prop-2-enyl ether failed to give any rearrangement products.[6] Hydrolyses of (**21**) gave the 5-fluorouracil derivative (**23**).



(**21**)



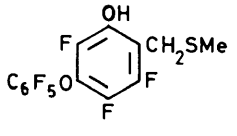
(**22**)



(**23**)

The work described in this paper has shown that dearomatisation of monocyclic, polycyclic, and heterocyclic ring systems can be effected under very mild conditions. We have also investigated the possibility of rearomatising some of the cyclohexa-2,4-dienone ring systems *via* reduction of the carbonyl group to a secondary alcohol and loss of HF from the α,β position to provide a novel route to *ortho*-substituted polyfluorophenolic compounds. In the absence of powerful overriding substituent effects, only *meta*-substituted products are to be expected by the more direct route involving nucleophilic displacement of fluorine in a polyfluorophenolic compound.[14]

Treatment of the cyclohexa-2,4-dienone (**2**) with sodium borohydride gave an extremely complex mixture of products which was not examined further, but compound (**3**) gave the phenol (**24**) (97%). The naphthalenone (**13**) and $NaBH_4$ gave the secondary alcohol (**25**) (88%) which was dehydrofluorinated by KOH to the naphthalenol derivative (**26**) (86%).



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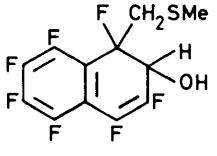

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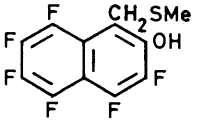
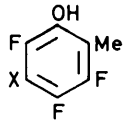


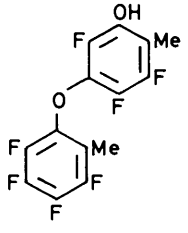
(26)

Attempted desulphurisations of the thiomethoxymethyl substituent in some of the cyclohexa-2,4-dienones was accompanied by loss of HF and further hydrogenation/tautomerism to give rearomatised products. Compound (**2**) gave the simple phenolic compound (**27**) (22%) accompanied by the mono- and di-ether compounds (**28**) (33%) and (**29**) (14%) respectively. Compound (**28**) is formed presumably *via* the preliminary reaction of (**27**) with (**2**) and a similar process between (**28**) and (**2**) would account for the formation of (**29**). When the substituent at C-3 in the cyclohexa-2,4-dienone was a poor leaving group, the reaction product was much simpler: the 3-methoxy compound (**4**) and Raney nickel gave (**30**) (98%). The desulphurisation-aromatisation reaction with the naphthalen-2(1*H*)-one (**13**) was also uncomplicated giving the 1-methylnaphthalen-2-ol (**31**) (99%).

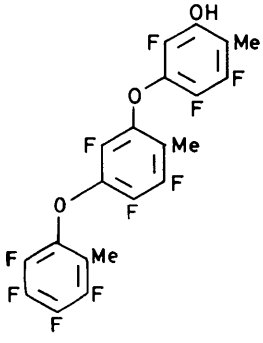


(27) X = F

(30) X = OMe



(28)



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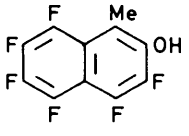
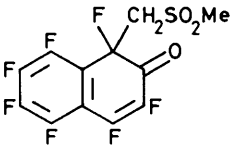


(31)

In view of the ready availability of the naphthalen-2-one (**13**), we oxidised the sulphide group with peroxytrifluoroacetic acid to give the sulphone (**32**) with a view to eliminating HF *via* the active methylene group to be followed by an electrocyclisation of (**33**) to give the heterocyclic compound (**34**). Treatment of (**32**) with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) gave two



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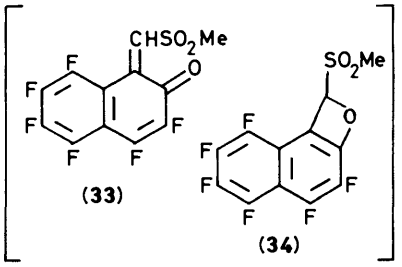
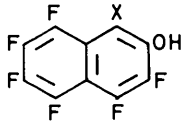


(33) (34)



(35) X = CHO

(36) X = $CH(SO_2Me)_2$

compounds: the hydroxy aldehyde (**35**) (76%) and the bis-(methylsulphonyl) derivative (**36**) (5%). A rationalisation for the formation of both these products follows the proposal submitted to account for the isolation of (**17**) and (**18**) from 2,4,5,6-tetrafluoropyridin-3-ol: formation of (**33**), then hydration and hydrolysis to give (**35**), while the released $MeSO_2^-$ could attack (**33**) to give (**36**).

Experimental

^1H (60 MHz) and ^{19}F N.m.r. (56.4 MHz) spectra were obtained with a Varian EM360L spectrometer or ^1H (250 MHz) and ^{19}F (235 MHz) spectra with a Bruker AC250. Chemical shifts are downfield from internal TMS (δ_H), or upfield from internal $CFCl_3$ (δ_F). Mass spectroscopy data were obtained with a VG 7070E instrument. Molecular ions M^+ are quoted for electron ionisation except where stated: c.i. represents chemical ionisation using isobutane.

Reactions of Polyfluoroarenols with Dimethyl Sulphoxide (DMSO), Dicyclohexylcarbodi-imide (DCC) and Orthophosphoric Acid.—(a) *With pentafluorophenol.* A mixture of pentafluorophenol (1.03 g, 5.6 mmol) anhydrous DMSO (100 ml), benzene (100 ml), and DCC (4.65 g, 22.6 mmol) was cooled to 0 °C and anhydrous orthophosphoric acid in DMSO (5M; 0.7 ml) was added to the stirred solution. After a short induction period there was a mild exothermic reaction with dicyclohexylurea (DCU) being precipitated. The reaction temperature was maintained at ≤ 12 °C over 1 h and after a further 16 h at room temperature the mixture was diluted with ether, the DCU removed by filtration, and the filtrate washed with water. The organic phase was dried ($MgSO_4$), the solvents evaporated, and the residue further evaporated under reduced pressure (0.05

mmHg) into a trap cooled in liquid air. The volatile mixture was separated by chromatography on silica using $CHCl_3/CCl_4$ (1:1 v/v) to give two components: (i) a liquid, *pentafluorophenylmethylthiomethyl ether* (**1**) (0.081 g, 6%) [Found: C, 39.1; H, 2.35%; M^+, 244 (c.i.). $C_8H_5F_5OS$ requires C, 39.35; H, 2.06%; *M*, 244]; δ_F (neat liquid, external $CFCl_3$) 151.1 (2-F, 6-F), 158.3 (4-F), and 159.8 p.p.m. (3-F, 5-F); δ_H ($CDCl_3$, external TMS) 1.92 (s, CH_3) and 4.88 (s, CH_2); and (ii) a pale yellow liquid, 2,3,4,5,6-*pentafluoro*-6-*methylthiomethylcyclohexa*-2,4-*dienone* (**2**) (0.173 g, 13%), b.p. 40 °C/0.05 mmHg (Found: C, 39.45; H, 2.05; M^+, 244. $C_8H_5F_5OS$ requires C, 35.35; H, 2.06%; *M*, 244); δ_F (Et_2O) 132.2 (nm, 3-F), 141.0 (bd, 6-F), 142.2 (ddd, 5-F), 156.8 (nm, 4-F) and 159.4 p.p.m. (ddt, 2-F), $J_{2\text{-F},3\text{-F}}$ 3.5 Hz, $J_{2\text{-F},4\text{-F}}$ 3.5 Hz, $J_{2\text{-F},5\text{-F}}$ 22 Hz, $J_{2\text{-F},6\text{-F}}$ 13 Hz, $J_{4\text{-F},5\text{-F}}$ 6 Hz, and $J_{5\text{-F},6\text{-F}}$ 35 Hz; δ_H($CDCl_3$) 2.02 (CH_3) and 3.18 (CH_2).

The residual involatile material from the reaction was crystallised at low temperature from light petroleum (b.p. 40—60 °C) to give the yellow 2,4,5,6-*tetrafluoro*-6-*methylthiomethyl*-3-*pentafluorophenoxycyclohexa*-2,4-*dienone* (**3**) (0.415 g, 36%), m.p. 32.5—33.5 °C (Found: C, 41.15; H, 1.0%; M^+, 408. $C_{14}H_5F_9O_2S$ requires C, 41.19; H, 1.23%; *M*, 408); δ_F(Et_2O) 141.3 (bd, 6-F), 142.5 (ddd, 5-F), 154.1 (dd, 4-F), 156.1 (d, 2′-F, 6′-F), 157.9 (ddd, 2-F), 158.2 (t, 4′-F), and 162.1 p.p.m. (t, 3′-, 5′-F), $J_{2\text{-F},4\text{-F}}$ 1.5 Hz, $J_{2\text{-F},5\text{-F}}$ 20.5 Hz, $J_{2\text{-F},6\text{-F}}$ 12 Hz, $J_{4\text{-F},5\text{-F}}$ 4 Hz, and $J_{5\text{-F},6\text{-F}}$ 35 Hz; δ_H($CDCl_3$) 2.12 (CH_3) and 3.26 (CH_2).

(b) *With* 2,3,5,6-*tetrafluorophenol*. A mixture of 2,3,5,6-tetrafluorophenol (1.372 g, 8.3 mmol), anhydrous DMSO (20 ml), benzene (20 ml), and DCC (4.46 g, 21.6 mmol) was treated with orthophosphoric acid in DMSO (5M; 1.2 ml) and worked up as in (a) to give two products: (i) *methylthiomethyl* 2,3,5,6-*tetrafluorophenyl ether* (**7**) (0.151 g, 8%) [Found: C, 42.7; H, 2.75%; M^+, 226 (c.i.). $C_8H_6F_4OS$ requires C, 42.48; H, 2.67%; *M*, 226]; δ_F (neat liquid) 142.3 and 157.6 p.p.m. from external $CFCl_3$ in the ratio 1:1; δ_H (neat liquid) 1.95 (CH_3), 5.0 (CH_2) and 6.5 (4-H) from external TMS; and (ii) the pale yellow 2,3,5,6-*tetrafluoro*-6-*methylthiomethylcyclohexa*-2,4-*dienone* (**8**) (1.297 g, 69%) [Found: C, 42.75; H, 2.3%; M^+, 226 (c.i.). $C_8H_6F_4OS$ requires C, 42.48; H, 2.67%; *M*, 226]; δ_F($CDCl_3$) 106.0 (ddt, 5-F), 112.6 (m, 3-F), 146.6 (dm, 6-F) and 163. 6 p.p.m. (m, 2-F), $J_{2\text{-F},3\text{-F}}$ 7.5 Hz, $J_{2\text{-F},5\text{-F}}$ 23 Hz, $J_{2\text{-F},6\text{-F}}$ 13 Hz, $J_{3\text{-F},5\text{-F}}$ 7 Hz, $J_{3\text{-F},6\text{-F}}$ 5 Hz, $J_{4\text{-H},5\text{-F}}$ 9 Hz, and $J_{5\text{-F},6\text{-F}}$ 36 Hz; δ_H ($CDCl_3$) 2.10 (CH_3), 3.21 (CH_2), and 6.16 (4-H), $J_{2\text{-F},4\text{-H}}$ 5 Hz, and $J_{3\text{-F},4\text{-H}}$ 9.5 Hz.

(c) *With* 1,3,4,5,6,7,8-*heptafluoro*-2-*naphthol*. A mixture of the naphthol (1.075 g, 4.0 mmol), anhydrous DMSO (12 ml), benzene (12 ml), and DCC (3.42 g, 16.6 mmol) was treated with orthophosphoric acid in DMSO (5M; 0.4 ml) for 21 h at room temperature and the two involatile products were separated by chromatography on silica–CCl_4 to give two products: (i) 1,3,4,5,6,7,8-*heptafluoro*-2-*naphthyl methylthiomethyl ether* (**12**) (0.126 g, 10%), m.p. 45—46.5 °C [from light petroleum (b.p. 40—60 °C)] (Found: C, 43.7; H, 1.5%; M^+, 330. $C_{12}H_5F_7OS$ requires C, 43.64; H, 1.53%; *M*, 330); δ_F($CDCl_3$) 138.2 (dm), 145.7—148.4 (overlapping m), and 156.4 p.p.m. (overlapping m) in the ratio 1:4:2; δ_H($CDCl_3$) 2.38 (CH_3) and 5.38 (CH_2); and (ii) 1,3,4,5,6,7,8-*heptafluoro*-1-*methylthiomethylnaphthalen*-2(1H)-*one* (**13**) (0.943 g, 72%), m.p. 90.5—91 °C [from light petroleum (b.p. 80—100 °C)] (Found: C, 43.5; H, 1.35%; M^+, 330. $C_{12}H_5F_7OS$ requires C, 43.64; H, 1.53%; *M*, 330); δ_F($CDCl_3$) 122.2 (dm, 4-F), 135.0 (m, 8-F), 138.8 (dm, 5-F), 141.5 (dm, 1-F), 148.9 and 150.1 (m, m, 6-F, 7-F), and 156.5 (m, 3-F); $J_{4\text{-F},5\text{-F}}$ 76 Hz, and $J_{1\text{-F},8\text{-F}}$ 19 Hz; δ_H($CDCl_3$) 1.96 (CH_3), 3.29 and 3.57 (AB, CH_2), J_{AB} 13 Hz, $J_{1\text{-F},H_A}$ 7.5 Hz, and $J_{1\text{-F},H_B}$ 6.5 Hz.

Reactions of Polyfluoro-arenols and -heteroarenols with DMSO, Trifluoroacetic Anhydride (TFAA), and Triethylamine (TEA).—(a) *With pentafluorophenol*. A mixture of DMSO (4 ml) and dry methylene dichloride (30 ml) was cooled to −60 °C in solid CO_2–acetone and TFAA (3.9 ml, 28 mmol) was added dropwise to the stirred solution whereupon a white solid precipitated. Pentafluorophenol (2.438 g, 13 mmol) in dry methylene dichloride (30 ml) was added dropwise to the mixture, the temperature being maintained at ≤ −50 °C. After 2 h, TEA (6.5 ml, 47 mmol) was added and the solution was allowed to warm to room temperature over 18 h. The mixture was diluted with ether, washed with water and with hydrochloric acid (2M), and the organic phase dried ($MgSO_4$). Careful evaporation of the solvents under reduced pressure and examination of the residue by ^{19}F n.m.r. spectroscopy showed the presence of only two products which were separated by chromatography on silica using $CHCl_3$–CCl_4 (1:1 v/v) to give the dienone (**1**) (2.364 g, 73%) and its 3-pentafluorophenoxy derivative (**3**) (0.456 g, 8%).

(b) *With* 1,3,4,5,6,7,8-*heptafluoro*-2-*naphthol*. The naphthol (0.946 g, 3.5 mmol) in dry CH_2Cl_2 (15 ml) was added dropwise to a mixture of DMSO (1 ml), dry CH_2Cl_2 (15 ml), and TFAA (1 ml, 7.1 mmol) at ≤ −55 °C followed after 2 h by the addition of TEA (1.5 ml, 11 mmol). The subsequent procedure reported in (a) was repeated and the two components present were separated by chromatography on silica using CCl_4 to give, on elution with ether, the naphthalen-2(1*H*)-one (**13**) (0.898 g, 78%), followed by unchanged naphthol (0.065 g, 7%).

(c) *With* 4-*bromo*-3,5,6-*fluoropyridin*-2-*ol*. The pyridin-2-ol derivative (0.588 g, 2.6 mmol) in dry CH_2Cl_2 (10 ml) was added dropwise to a mixture of DMSO (0.8 ml), dry CH_2Cl_2 (10 ml), and TFAA (0.8 ml, 5.7 mmol) at ≤ −50 °C followed after 2 h by the addition of TEA (1.25 ml, 9.0 mmol). The crude reaction product, worked up as in (a) contained four components by ^{19}F n.m.r. spectroscopic analysis, one of which was the unchanged pyridin-2-ol (0.129 g, 22%); this was isolated by washing the products in ether with dilute aqueous $NaHCO_3$, acidification, and extraction with ether. Evaporation of the dried ($MgSO_4$) ether solution of the remaining three components and chromatography on silica using CCl_4–ethyl acetate (80:20, v/v) gave the three remaining compounds as they eluted from the column: (i) 4-*bromo*-3,5,6-*trifluoro*-2-*pyridylmethylthiomethyl ether* (**14**) (0.011 g, 1.5%) m.p. 48—50 °C (Found: C, 29.4; H, 1.5; N, 4.5%; M^+, 287/289. $C_7H_5BrF_3NOS$ requires C, 29.18; H, 1.75; N, 4.86%; *M*, 287/289); δ_F($CDCl_3$) 91.6 (6-F), 134.7 (3-F), and 143.3 p.p.m. (5-F); δ_H($CDCl_3$) 2.30 (CH_3) and 5.48 (CH_2); (ii) 4-*bromo*-3,5-*difluoro*-3-*methylthiomethylpyridin*-2,6(1H,3H)-*dione* (**15**) (0.061 g, 8%), m.p. 139.5—140 °C [by sublimation at 100 °C/0.05 mmHg and recrystallisation from light petroleum (b.p. 100—120 °C)] (Found: C, 29.4; H, 2.4; N, 4.6%; M^+, 285/287. $C_7H_6BrF_2NO_2S$ requires C, 29.39; H, 2.11; N, 4.90%; *M*, 285/287); δ_F([$^2H_6$]acetone) 114.6 (5-F) and 133.0 p.p.m. (3-F); δ_H([$^2H_6$]acetone) 2.15 (CH_3), 3.35 (CH_2) and 6.36 (NH); and (iii) 4-*bromo*-3,5,6-*trifluoro*-6-*methylthiomethylpyridin*-2(1H)-*one* (**16**) (0.327 g, 44%), m.p. 75—76 °C (from diethyl ether) (Found: C, 29.4; H, 1.6; N, 4.9%; M^+, 287/289. $C_7H_5BrF_3NOS$ requires C, 29.18; H, 1.75; N, 4.86%; *M*, 287/289); δ_F($CDCl_3$) 122.3 (dm, 6-F), 128.5 (dd, 5-F), and 166.3 p.p.m. (t, 3-F); δ_H($CDCl_3$) 2.3 (s, CH_3) and 5.2 (d, CH_2), $J_{6\text{-F},NCH_2}$ 4 Hz, $J_{6\text{-F},3\text{-F}}$ 19 Hz, $J_{6\text{-F},3\text{-F}}$ 9.5 Hz, $J_{3\text{-F},5\text{-F}}$ 9.5 Hz.

(d) *With* 2,4,5,6-*tetrafluoropyridin*-3-*ol*. The pyridin-3-ol derivative (1.584 g, 9.5 mmol) in dry CH_2Cl_2 (30 ml) was added dropwise to a mixture of DMSO (2.4 ml), dry CH_2Cl_2 (30 ml), and TFAA (2.6 ml; 18.5 mmol) at ≤ −50 °C followed after 2 h by the addition of TEA (4 ml, 29.0 mmol). The crude reaction product, worked up as in (a) was shown by ^{19}F n.m.r. spectroscopy to be a complex mixture. Evaporation of the mixture at room temperature/0.05 mmHg for 1.5 h into a trap cooled in liquid air removed two components which were separated by chromatography on silica using CH_2Cl_2 to give (i) 3-*hydroxy*-

4,5,6-*trifluoropyridine*-2-*carbaldehyde* (**17**) (0.102 g, 6%), m.p. 63—64 °C [from light petroleum (b.p. 30—40 °C) at low temperature] [Found: C, 40.65; H, 1.05; N, 7.6%; M^+, 177 (c.i.). $C_6H_2F_3NO_2$ requires C, 40.69; H, 1.14; N, 7.91%; *M*, 177]; $\delta_F(CDCl_3)$ 87.65 (6-F), 138.8 (4-F), and 148.6 p.p.m. (5-F); $\delta_H(CDCl_3)$ 9.86 (CHO) and 10.94 (OH); and (ii) unchanged starting material (0.203 g, 13%).

The residue (0.801 g), involatile at room temperature, was sublimed at 70 °C/0.05 mmHg over 2 days and the sublimate was chromatographed on silica using CCl_4 initially, followed by CH_2Cl_2 to give 4,5,6-*trifluoro*-2-*di*(*methylthio*)*methylpyridin*-3-*ol* (**18**) (0.139 g, 6%), m.p. 70—71 °C [from light petroleum (b.p. 40—60 °C)] [Found: C, 37.5; H, 3.4; N, 5.5%; M^+, 208. $C_8H_8F_3NOS_2$ requires C, 37.64; H, 3.16; N, 5.49%; $M - 47$ (CH_3S), 208]; $\delta_F(CDCl_3)$ 90.8 (6-F), 139.3 (4-F), and 161.0 p.p.m. (5-F; $\delta_H(CDCl_3)$ 2.19 [$(SCH_3)_2$], 5.01 (CH), and 7.17 (OH).

(e) *With* 2,3,5,6-*tetrafluoropyridin*-4-*ol*. The pyridin-4-ol derivative used in a procedure analogous to that described in (a), failed to undergo *any* reaction; only unchanged starting material was recovered from the experiment.

(f) *With* 2,5,6-*trifluoropyrimidin*-4-*ol*. The pyrimidin-4-ol (1.056 g, 7.0 mmol) in dry CH_2Cl_2 (15 ml) was added dropwise to a mixture of DMSO (1.6 ml) in dry CH_2Cl_2 (15 ml) and TFAA (1.9 ml, 13.5 mmol) at ≤ -50 °C followed after 2 h by the addition of TEA (1.9 ml, 14.0 mmol). The crude product, worked up as in (a) was separated by chromatography on silica using $CHCl_3$ into two components: (i) 2,5,6-*trifluoro*-3-*methylthiomethylpyrimidin*-4(3H)-*one* (**21**) (1.051 g, 71%), m.p. 66—67 °C [from light petroleum (b.p. 40—60 °C)] (Found: C, 34.2; H, 2.55; N, 13.15%; M^+, 210. $C_6H_5F_3N_2OS$ requires C, 34.28; H, 2.40; N, 13.33%; *M*, 210); $\delta_F(CDCl_3)$ 56.2 (2-F), 89.6 (6-F), and 172.4 p.p.m. (5-F); $\delta_H(CDCl_3)$ 2.30 (CH_3) and 5.10 (CH_2); $\lambda_{max.}$(cyclohexane) 216 (ε 4 900) and 266 nm (3 400) similar to the values for 3-allyl-2,5,6-trifluoropyrimidin-4(3*H*)-one;[6] and (ii) after elution with ether, the unchanged pyrimidin-4-ol derivative (0.198 g, 19%).

(g) *With* 5-*fluoro*-4,6-*dimethoxypyrimidin*-2-*ol*. The pyrimidin-2-ol derivative (0.437 g, 2.9 mmol) in dry CH_2Cl_2 (10 ml) was added dropwise to a mixture of DMSO (0.9 ml) in dry CH_2Cl_2 (10 ml) and TFAA (0.9 ml, 6.5 mmol) at ≤ -50 °C followed after 2 h by the addition of TEA (0.9 ml, 6.5 mmol). The crude product, worked up as in (a) was separated by chromatography on silica using CCl_4–ethyl acetate (1:1 v/v) into two components: (i) unchanged starting material (0.077 g, 18%); and (ii) after elution of the column with ether and sublimation at 90 °C/0.05 mmHg 5-*fluoro*-4,6-*dimethoxy*-1-*methylthiomethylpyrimidin*-2(1H)-*one* (**22**) (0.344 g, 59%), m.p. 103—105 °C (from toluene) (Found: C, 41.2; H, 4.45; N, 11.6%; M^+, 234 (c.i.). $C_8H_{11}FN_2O_3S$ requires C, 41.02; H, 4.73; N, 11.96%; *M*, 234); $\delta_F(CDCl_3)$ 191.3 p.p.m. (q, 5-F); $\delta_H(CDCl_3)$ 2.25 (SCH_3), 4.0 (s, OCH_3), 4.3 (d, OCH_3), and 5.0 (CH_2), $J_{5\text{-}F,OCH_3}$ 5 Hz.

Reaction of 2,3,4,5,6-*Pentafluoro*-6-*methylthiomethylcyclohexa*-2,4-*dienone* (**2**) *with Methanol*.—A mixture of the dienone (1.271 g), diethyl ether (10 ml), and methanol (7 ml) was stirred at room temperature for 3 h and then poured into water and extracted with ether. The dried ($MgSO_4$) extracts were evaporated and the residue evaporated at 50 °C/ 0.05 mmHg to give 2,4,5,6-*tetrafluoro*-3-*methoxy*-6-*methylthiomethylcyclohexa*-2,4-*dienone* (**4**) (1.269 g, 95%) as a liquid (Found: C, 41.9; H, 2.85%; M^+, 256. $C_9H_8F_4O_2S$ requires C, 42.19; H, 3.15%; *M*, 256); $\delta_F(CDCl_3)$ 142.0 (dm, 6-F), 144.9 (ddd, 5-F), 152.6 (nm, 4-F), and 167.2 p.p.m. (m, 2-F), $J_{2\text{-}F,5\text{-}F}$ 17 Hz, $J_{2\text{-}F,6\text{-}F}$ 9.5 Hz, $J_{4\text{-}F,5\text{-}F}$ 6.5 Hz, $J_{4\text{-}F,6\text{-}F}$ 3 Hz, and $J_{5\text{-}F,6\text{-}F}$ 34.5 Hz; $\delta_H(CDCl_3)$ 2.01 (CH_3S), 3.18 (CH_2), and 4.24 (d, CH_3O, $J_{2\text{-}F,CH_3O}$ 6.5 Hz.

Reactions of 2,3,5,6-*Tetrafluoro*-6-*methylthiomethylcyclohexa*-2,4-*dienone* (**8**).—(a) *With pentafluorophenol*. A mixture of the dienone (**8**) (0.265 g), pentafluorophenol (0.310 g), and potassium carbonate (0.1 g) was heated in tetrahydrofuran (15 ml) at 70 °C for 5 h; it was then diluted with water, acidified (2M H_2SO_4) and extracted with ether. The dried ($MgSO_4$) extracts were evaporated and the residue purified by chromatography on silica using CH_2Cl_2 to give 2,6-*difluoro*-3-*pentafluorophenoxy*-6-*methylthiomethylcyclohexa*-2,4-*dienone* (**10**) (0.395 g, 61%), m.p. 108—109.5 °C [from light petroleum (b.p. 80—100 °C)] (Found: C, 43.6; H, 1.2%; M^+, 554. $C_{20}H_6F_{12}O_3S$ requires C, 43.33; H, 1.09%; *M*, 554); $\delta_F(CDCl_3)$ 145.7 (bq, 6-F), 152.5 (d, 2′-F, 6′-F), 155.2 (d, 2″-F, 6″-F), 155.8 (t, 4′-F), 157.6 (t, 4″-F), 160.1 (t, 3′-F, 5′-F), 161.5 (t, 3″-F, 5″-F), and 165.0 p.p.m. (dd, 2-F), $J_{2\text{-}F,6\text{-}F}$ 12 Hz; $\delta_H(CDCl_3)$ 2.13 (CH_3), 3.26, 3.45 (AB, CH_2), 5.40 (d, 4-H), J_{AB} 12.5 Hz, $J_{2\text{-}F,4\text{-}F}$ 5 Hz, $J_{6\text{-}F,H_A}$ 6.5 Hz, and $J_{6\text{-}F,H_B}$ 8 Hz.

(b) *With liquid* HF. The dienone (**8**) (0.809 g) was added to liquid HF (*ca.* 20 ml) at room temperature in a PTFE beaker. After 17 h the mixture was diluted with water, extracted with ether, and the dried ($MgSO_4$) extracts evaporated. Chromatography of the residue on silica using CH_2Cl_2 gave two fractions: (i) a mixture of two components which was separated by evaporation under reduced pressure at room temperature/ 0.05 mmHg to give 2,3,5,6-tetrafluorophenol (0.111 g, 19%) identified by comparison of its i.r. with an authentic sample; the less volatile residue was sublimed at 50 °C/0.05 mmHg to give 2,3,5,6-*tetrafluoro*-4-*methylthiomethylphenol* (**9**) (0.252 g, 31%), m.p. 77—78 °C [from light petroleum (b.p. 60—80 °C)] [Found: C, 42.7; H, 2.3%; M^+, 226 (c.i.). $C_8H_6F_4OS$ requires C, 42.48; H, 2.67%; *M*, 226]; $\delta_F(CDCl_3)$ at 145.5 and 163.7 p.p.m. in the ratio 1:1; $\delta_H(CDCl_3)$ 2.14 (CH_3), 3.74 (CH_2), and 5.86 (OH); and (ii) a single component, 2,3,5,6-*tetrafluoro*-4-*hydroxyphenylmethanol* (**11**) (0.095 g, 14%), m.p. 116.5—117 °C (from benzene) [Found: C, 42.9; H, 1.8%; M^+, 178. $C_7H_4F_4O_2$ requires C, 42.87; H, 2.06%; $M - 18$ (H_2O), 178]; $\delta_F([^2H_6]$acetone) at 148.3 and 164.0 p.p.m. in the ratio 1:1; $\delta_H([^2H_6]$acetone) 4.50 (m, C–OH), 4.67 (CH_2), and 10.0 (s, OH).

Reactions of some Rearrangement Products with Sodium Borohydride.—(a) 2,4,5,6-*Tetrafluoro*-3-*pentafluorophenoxy*-6-*methylthiomethylcyclohexa*-2,4-*dienone* (**3**). A solution of the dienone (**3**) (0.170 g) in methanol (5 ml) was treated with sodium borohydride (0.031 g) in methanol (2 ml) at room temperature for 30 min. The mixture was acidified (2M H_2SO_4) and extracted with ether. The dried ($MgSO_4$) extracts were evaporated and the residue sublimed at 70 °C/0.05 mmHg to give 2,4,5-*trifluoro*-6-*methylthiomethyl*-3-*pentafluorophenoxyphenol* (**24**) (0.158 g, 97%), m.p. 107—108 °C [from light petroleum (b.p. 80—100 °C] (Found: C, 43.35; H, 1.2%; M^+, 390. $C_{14}H_6F_8O_2S$ requires C, 43.09; H, 1.55%; *M*, 390); $\delta_F(Et_2O)$ 146.2 (dd, 5-F), 157.9 (d, 2′-F, 6′-F), 158.9 (b, 2-F), 162.7 (t, 4′-F), 164.4 (t, 3′-F, 5′-F), and 166.3 p.p.m. (d, 4-F), $J_{2\text{-}F,5\text{-}F}$ 9 Hz and $J_{4\text{-}F,5\text{-}F}$ 21 Hz; $\delta_H(CDCl_3)$ 2.10 (CH_3), 3.78 (CH_2), and 6.2 (OH).

(b) 1,3,4,5,6,7,8-*Heptafluoro*-1-*methylthiomethylnaphthalen*-2(1H)-*one* (**13**). The naphthalen-2(1*H*)-one was treated with sodium borohydride under conditions similar to those in (a) to give an equimolar mixture of racemic diastereoisomers 1,3,4,5,6,7,8-*heptafluoro*-2,3-*dihydro*-1-*methylthiomethylnaphthalen*-2-*ol* (**25**) (88%), m.p. 103—104 °C [from light petroleum (b.p. 40—60 °C)] (Found: C, 43.7; H, 1.85%; M^+, 332. $C_{12}H_7F_7OS$ requires C, 43.38; H, 2.12%; *M*, 332); $\delta_F(CDCl_3)$ 134.5 (m, 8-F), 142.6 (dm, 5-F), 144.0 (m, 3-F), 147.1 (m, 1-F), 151.1 (dm, 4-F), 151.2 and 152.7 p.p.m. (both t, 6-F, 7-F), $J_{4\text{-}F,5\text{-}F}$ 62 Hz and $J_{1\text{-}F,8\text{-}F}$ 21 Hz; $\delta_H(CDCl_3)$ 2.24 (CH_3), 2.83 and 2.86 (OH), 3.36, 3.60 (AB of CH_2, J_{AB} 15 Hz), 3.25 3.54 (A′B′ of CH_2, $J_{A'B'}$ 16 Hz), and 5.23 (m, CH).

Compound (**25**) (0.078 g) was treated with KOH (0.1 g) in

tetrahydrofuran (7 ml) under reflux to give 3,4,5,6,7,8-*hexafluoro*-1-*methylthiomethyl*-2-*naphthol* (**26**) (0.063 g, 86%), m.p. 125.5—126 °C [from light petroleum (b.p. 80—100 °C)] (Found: C, 46.4; H, 1.8%; M^+, 312. $C_{12}H_6F_6OS$ requires C, 46.16; H, 1.94%; *M*, 312); $\delta_F(CDCl_3)$ 142.4 (m, 8-F), 143.1 (dd, 4-F), 146.2 (dt, 5-F), 155.8, 159.1 (t and t, 6-F, 7-F) and 157.0 p.p.m. (m, 3-F); $\delta_H(CDCl_3)$ 2.11 (CH_3), 4.26 (CH_2), and 6.2 (OH).

Reactions of some Rearrangement Products with Raney Nickel.—(a) 2,3,4,5,6-*Pentafluoro*-6-*methylthiomethylcyclohexa*-2,4-*dienone* (**2**). The dienone (**2**) (0.541 g), tetrahydrofuran, and Raney nickel (*ca.* 4 g) were stirred under nitrogen at room temperature for 24 h. The mixture was filtered through a layer of $MgSO_4$, the filtrate evaporated, and the residue further evaporated at room temperature/0.05 mmHg to give 2,3,4,5-*tetrafluoro*-6-*methylphenol* (**27**) (0.087 g, 22%), m.p. 22—23 °C (Found: C, 46.8; H, 2.4%; M^+, 180. $C_7H_4F_4O$ requires C, 46.68; H, 2.24%; *M*, 180); $\delta_F(CDCl_3)$ 144.6 (dd, 5-F), 161.8 (t, 3-F), 167.3 (dm, 2-F), and 169.8 p.p.m. (td, 4-F); $\delta_H(CDCl_3)$ 2.24 (CH_3) and 5.22 (OH). The less volatile material was sublimed at 50 °C/0.05 mmHg and the sublimate recrystallised from light petroleum (b.p. 30—40 °C) to give 2,3,4,5-*tetrafluoro*-6-*methylphenyl* 2′,3′,6′-*trifluoro*-5′-*hydroxy*-4′-*methylphenyl ether* (**28**) (0.125 g, 33%) (Found: C, 49.7; H, 2.1%; M^+, 340. $C_{14}H_7F_7O_2$ requires C, 49.42; H, 2.07%; *M*, 340); $\delta_F(CDCl_3)$ 143.2 (dm, 3′-F) 144.9 (dm, 5-F), 158.1 (dm, 2-F), 159.8 and 162.4 (both t, 3-F, 4-F), 162.0 (nm, 6′-F) and 164.8 p.p.m. (d, 2′-F), $J_{2\text{-}F,3\text{-}F}$ 21 Hz, $J_{3\text{-}F,4\text{-}F}$ 21 Hz, $J_{4\text{-}F,5\text{-}F}$ 21 Hz and $J_{2'\text{-}F,3'\text{-}F}$ 21 Hz; $\delta_H(CDCl_3)$, 2.18, 2.28 (2 × CH_3) and 5.17 (OH). The least volatile material was sublimed at 100 °C/0.05 mmHg and recrystallised from light petroleum (b.p. 60—80 °C) to give 2,3,6-*trifluoro*-4-*methyl*-1-(2′,3′,4′,5′-*tetrafluoro*-6-*methylphenoxy*)-5-(2″,3″,6″-*trifluoro*-5″-*hydroxy*-4-*methylphenoxy*)*benzene* (**29**) (0.051 g, 14%) (Found: C, 50.1; H, 1.75%; M^+, 500. $C_{21}H_{10}F_{10}O_3$ requires C, 50.41; H, 2.01%; *M*, 500); $\delta_F(CDCl_3)$ 142.9, 143.4 (both ddd, 3-F, 3″-F), 144.8 (ddd, 5′-F), 152.6 (dm, 6-F), 157.1 (dd, 2-F), 158.3 (dm, 2′-F), 159.5, 162.1 (both t, 3′-F, 4′-F), 162.3 (nm, 6″-F), and 165.0 p.p.m. (dm, 2″-F), $J_{2\text{-}F,3\text{-}F}$ 22 Hz, $J_{2''\text{-}F,3''\text{-}F}$ 22 Hz, $J_{2'\text{-}F,3'\text{-}F}$ 22 Hz, $J_{3'\text{-}F,4'\text{-}F}$ 22 Hz, $J_{4'\text{-}F,5'\text{-}F}$ 22 Hz, $J_{3\text{-}F,6\text{-}F}$ 9 Hz, $J_{2'\text{-}F,5'\text{-}F}$ 9 Hz, and $J_{3''\text{-}F,6''\text{-}F}$ 9 Hz; $\delta_H(CDCl_3)$ 2.27, 2.29, and 2.30 (3 × CH_3), and 5.18 (OH).

(b) 2,4,5,6-*Tetrafluoro*-3-*methoxy*-6-*methylthiomethylcyclohexa*-2,4-*dienone* (**4**). The dienone (**4**) was treated with Raney nickel as in (a) to give 2,4,5-*trifluoro*-3-*methoxy*-6-*methylphenol* (**30**) (98%), m.p. 72.5—73.5 °C [from light petroleum (b.p. 40—60 °C)] (Found: C, 50.3; H, 3.45%; M^+, 192. $C_8H_7F_3O_2$ requires C, 50.01; H, 3.67%; *M*, 192); $\delta_F(CDCl_3)$ 146.3 (dd, 5-F), 162.6 (d, 2-F), and 165.1 p.p.m. (d, 4-F), $J_{2\text{-}F,5\text{-}F}$ 10 Hz, $J_{4\text{-}F,5\text{-}F}$ 22 Hz; $\delta_H(CDCl_3)$ 2.16 (CH_3), 4.00 (CH_3O), and 5.17 (OH).

(c) 1,3,4,5,6,7,8-*Heptafluoro*-1-*methylthiomethylnaphthalen*-2(1H)-*one* (**13**). The naphthalen-2(1*H*)-one (**13**) was treated with Raney nickel as in (a) to give 3,4,5,6,7,8-*hexafluoro*-1-*methyl*-2-*naphthol* (**31**) (99%), m.p. 90—90.5 °C [from light petroleum (b.p. 40—60 °C)] (Found: C, 49.9; H, 1.6%; M^+, 266. $C_{11}H_4F_6O$ requires C, 49.64; H, 1.51%; *M*, 266); $\delta_F(CDCl_3)$ 143.4 (m, 8-F), 148.15, 148.60 (AB, 4-F, 5-F), 154.7 (m, 3-F), 159.8, 162.3 (both t, 6-F, 7-F), $J_{4\text{-}F,5\text{-}F}$ 64 Hz; $\delta_H(CDCl_3)$ 2.62 (CH_3) and 5.65 (OH).

Oxidation of 1,3,4,5,6,7,8-*Heptafluoro*-1-*methylthiomethylnaphthalen*-2(1H)-*one* (**13**).—Peroxytrifluoroacetic acid, prepared by the addition of hydrogen peroxide (30% w/v; 1 ml) to trifluoroacetic anhydride (7 ml), was added dropwise with stirring to the naphthalen-2(1*H*)-one (0.612 g) in CH_2Cl_2 (20 ml) at ≤10 °C. The mixture was stirred at room temperature for 19 h, diluted with water, and extracted with ether. The ether extracts were dried ($MgSO_4$) and evaporated and the residue sublimed at 100 °C/0.05 mmHg to give 1,3,4,5,6,7,8-*heptafluoro*-1-*methylsulphonylmethylnaphthalen*-2(1H)-*one* (**32**) (0.602 g, 90%), m.p. 127—127.5 °C (from chloroform) (Found: C, 40.0; H, 1.15%; M^+, 362. $C_{12}H_5F_7O_3S$ requires C, 39.79; H, 1.39%; *M*, 362).

Reaction of 1,3,4,5,6,7,8-*Heptafluoro*-1-*methylsulphonylmethylnaphthalen*-2(1H)-*one* (**32**) *with* 1,8-*Diazabicyclo*[5.2.0]-*undec*-7-*ene* (*DBU*).—A solution of the naphthalen-2(1*H*)-one (**32**) (1.029 g, 2.8 mmol) in dry tetrahydrofuran (40 ml) was treated at −60 °C with DBU (0.45 ml, 3 mmol) and maintained at this temperature for 2 h. The mixture was diluted with water, acidified (2M HCl), and extracted with ether and the dried ($MgSO_4$) extracts were evaporated. The residue was chromatographed on silica using $CHCl_3$ to give three components: (i) 3,4,5,6,7,8-*hexafluoro*-2-*hydroxynaphthalene*-1-*carbaldehyde* (**35**) (0.602 g, 76%), m.p. 90—92 °C [from light petroleum (b.p. 40—60 °C)] [Found: C, 47.35; H, 0.4%; M^+, 280 (c.i.). $C_{11}H_2F_6O_2$ requires C, 47.16; H, 0.72%; *M*, 280]; $\delta_F(CDCl_3)$ 128.0 (dd, 4-F), 137.9 (tm, 8-F), 143.2 (dm, 5-F), 151.2, 157.9 (both t, 6-F, 7-F), and 156.1 p.p.m. (m, 3-F), $J_{4\text{-}F,5\text{-}F}$ 72 Hz; $\delta_H(CDCl_3)$ 10.74 (CHO) and 14.48 (OH); (ii) unchanged starting material (**32**) (0.032 g, 3%); and after elution with diethyl ether and sublimation at 140 °C/0.05 mmHg, (iii) 3,4,5,6,7,8-*hexafluoro*-1-*di*(*methylsulphonyl*)*methylnaphthalen*-2-*ol* (**36**) (0.056 g, 5%) (from toluene), m.p. 180—181 °C (decomp.) [Found: C, 37.0; H, 1.6%; $M^+ - CH_3SO_2$ 343 (c.i.). $C_{13}H_8F_6O_5S_2$ requires C, 36.97; H, 1.91%; *M*, 422]; $\delta_F([^2H_6]$-acetone) 139.5 (dd, 4-F), 140.1 (dt, 8-F), 146.3 (dm, 5-F), 153.6 (m, 3-F), 155.3 and 160.3 p.p.m. (both t, 6-F, 7-F), $J_{4\text{-}F,5\text{-}F}$ 73 Hz; $\delta_H([^2H_6]$acetone) 3.39 (s, 2 × CH_3), 6.68 (d, CH), and 11.6 (OH), $J_{CH,8-F}$ 19 Hz.

Hydrolysis of 2,5,6-*Trifluoro*-3-*methylthiomethylpyrimidin*-4(3H)-*one* (**21**).—A mixture of the pyrimidin-4(3*H*)-one (**21**) (0.22 g), acetone (15 ml), and aqueous sodium hydroxide (2M; 1.1 ml) was stirred at room temperature for 2.5 h; it was then diluted with water, acidified (2M H_2SO_4), and extracted with ether. The extracts were dried ($MgSO_4$) and evaporated and the residue sublimed at 90 °C/0.05 mmHg to give 5,6-*difluoro*-3-*methylthiomethyl*-2,4(1H,3H)-*dione* (**23**) (0.197 g, 90%), m.p. 103—104 °C (from toluene) [Found: C, 34.9; H, 2.8; N, 13.1%; M^+, 208 (c.i.). $C_6H_6F_2N_2O_2S$ requires C, 34.61; H, 2.90; N, 13.46%; *M*, 208]; $\delta_F(CDCl_3)$ 115.3 (d, 6-F) and 187.6 p.p.m. (d, 5-F), $J_{5\text{-}F,6\text{-}F}$ 7.5 Hz; $\delta_H(CDCl_3)$ 2.30 (CH_3), 5.00 (CH_2), and 10.7 (NH).

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References

1 G. M. Brooke, R. S. Matthews, and N. S. Robson, *J. Fluorine Chem.*, 1980, **16**, 461.
2 G. M. Brooke, R. S. Matthews, and N. S. Robson, *J. Chem. Soc., Perkin Trans. 1*, 1980, 102.
3 G. M. Brooke and G. Plews, *J. Fluorine Chem.*, 1986, **34**, 59.
4 G. M. Brooke, J. R. Cooperwaite, and A. G. Morpeth, *J. Chem. Soc., Perkin Trans. 1*, 1985, 2637.
5 G. M. Brooke and J. R. Cooperwaite, *J. Chem. Soc., Perkin Trans. 1*, 1985, 2643.
6 G. M. Brooke and J. A. K. J. Ferguson, *J. Chem. Soc., Perkin Trans. 1*, 1986, 515.
7 (*a*) K. E. Pfitzner, J. P. Marino, and R. A. Olofson, *J. Am. Chem. Soc.*, 1965, **87**, 4658; (*b*) M. G. Burdon and J. G. Moffatt, *ibid.*, 1965, **87**, 4656; (*c*) J. P. Marino, K. E. Pfitzner, and R. A. Olofson, *Tetrahedron*, 1971, **27**, 4181; (*d*) R. A. Olofson and J. P. Marino, *ibid.*, 1971, **27**, 2195.

8 L. S. Kobrina, V. N. Kovtonyuk, and G. G. Yakobson, *J. Org. Chem. USSR* (*Engl. Transl.*), 1977, **13**, 1331; R. R. Soelch, G. W. Mauer, and D. M. Lemal, *J. Org. Chem.*, 1985, **50**, 5845.
9 A. J. Mancuso and D. Swern, *Synthesis*, 1981, 165.
10 A. K. Sharma, T. Ku, A. D. Dawson, and D. Swern, *J. Org. Chem.*, 1975, **40**, 2758.
11 R. D. Chambers, J. Hutchinson, and W. K. R. Musgrave, *J. Chem. Soc., Suppl. 1*, 1964, 5634.
12 R. D. Chambers, J. Hutchinson, and W. K. R. Musgrave, *J. Chem. Soc.*, 1965, 5040.
13 R. E. Banks, D. S. Field, and R. N. Haszeldine, *J. Chem. Soc. C*, 1967, 1822.
14 J. Burdon, W. B. Hollyhead, and J. C. Tatlow, *J. Chem. Soc.*, 1965, 5152.

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