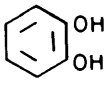
Polyhalogenoheterocyclic Compounds. Part 38.[1] Reactions of Fluorinated-Alkenes and -Cycloalkenes with Difunctional Nucleophiles

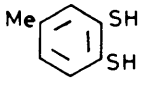
Andrew E. Bayliff, Martin R. Bryce, and Richard D. Chambers*
Department of Chemistry, University of Durham, South Road, Durham, DH1 3LE

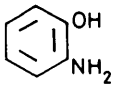
Reactions of fluorinated alkenes and cycloalkenes (**6**)—(**12**) with difunctional nucleophiles, *viz.* pyrocatechol, toluene-3,4-dithiol, *o*-aminophenol, and *o*-aminothiophenol, were found to give a range of heterocyclic products, generally in good yield, under mild conditions. A mechanistic rationalisation for product formation is contained.

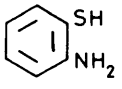
The reactions of a wide range of nucleophiles with fluorinated alkenes have been extensively studied,[2] but there are fewer reports in the literature concerning the formation of heterocyclic compounds by reactions of fluorinated alkenes with difunctional nucleophiles. Particularly noteworthy are studies involving enolate anions,[3] ethylene glycol,[4] and 2-amino-ethanol[5] with a variety of fluorinated alkenes and cycloalkenes. There are, however, only scattered publications[6] concerning the use, in this context, of disubstituted benzene derivatives.

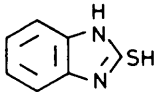
Possible mechanistic pathways for heterocyclisation of difunctional nucleophiles with fluoroalkenes are represented in the Scheme and, in view of the potential that the methodology offers for the synthesis of unusual heterocyclic systems, we have studied reactions of a range of aromatic difunctional nucleophiles with appropriate fluoro-alkenes and -cycloalkenes. The nucleophiles (**1**)—(**5**) and the alkenes (**6**)—(**12**) have been used in this study; simple perfluorinated alkenes are available commercially and the other fluorinated alkenes are obtained by oligomerisation procedures.[2a]

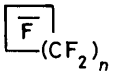

(1)

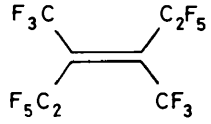

(2)

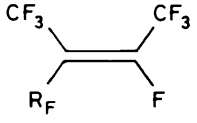

(3)

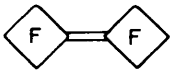

(4)

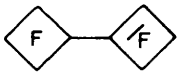

(5)

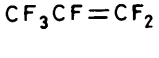

(6) $n = 1$
(7) $n = 2$


(8)
(mixture of *E* and *Z* isomers)


(9)
$R_F = (C_2F_5)_2CCF_3$


(10)


(11)

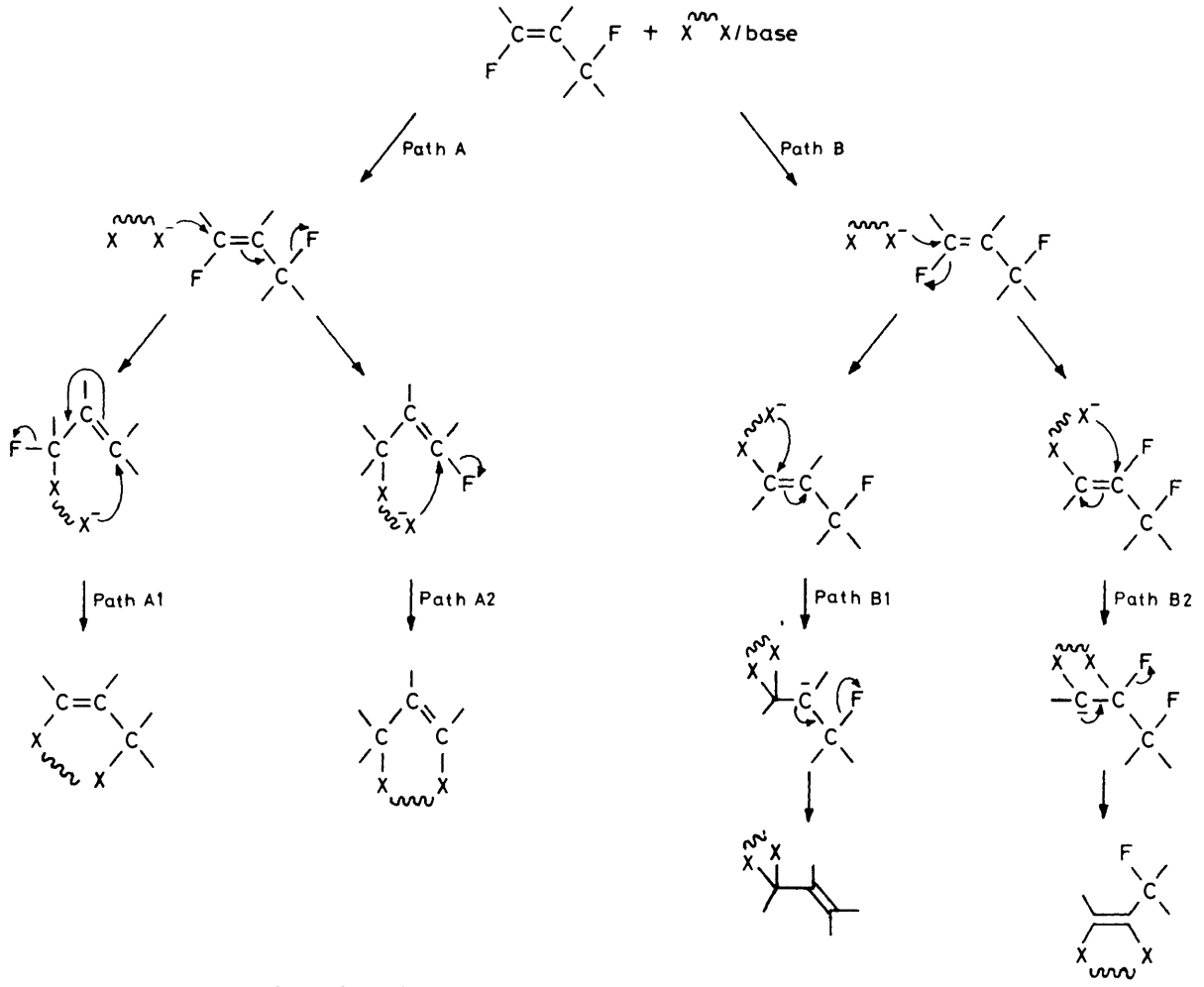

(12)

Reaction of pyrocatechol (**1**) with perfluoro-cyclobutene (**6**) and -cyclopentene (**7**) in the presence of potassium carbonate at room temperature gave the spiro acetals (**13**) and (**14**) respectively. The mechanism of reaction can be explained by Path B1 (see Scheme) involving initial nucleophilic displacement of fluoride ion from a vinylic site followed by cyclisation of the second oxygen with allylic displacement of fluoride. An alternative mechanism involving initial allylic displacement of fluoride can be discounted as the cyclisation step would then necessitate elimination of fluoride from a saturated site. An analogous product was obtained in low yield, along with other products, by Camaggi and Stephens from reaction of perfluoro-cyclohexene and ethylene glycol.[4c] The reason we find that pyrocatechol gives only spiro products (**13**) and (**14**) may be because pyrocatechol is more conformationally rigid than ethylene glycol.

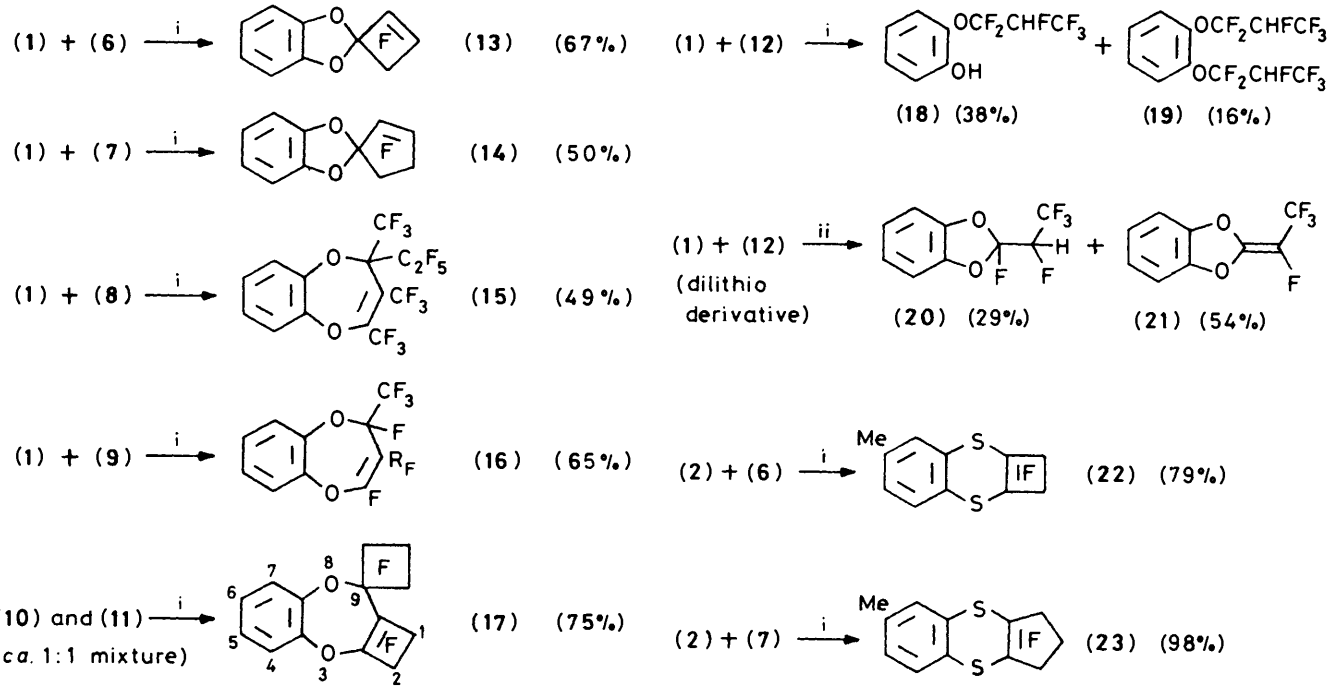
Reaction of pyrocatechol with the alkenes (**8**), (**9**), and a mixture of alkenes (**10**) and (**11**) followed a different course, giving 1,5-dioxepine derivatives (**15**), (**16**), and (**17**), respectively. The alkenes (**8**) and (**9**) react *via* Path A2 (see Scheme). Note that the fluorine atom lost in the initial vinylic displacement is from the CF_2 group, not the CF_3 group, thus avoiding formation of a terminal $=CF_2$ group. We have clearly shown that the alkene (**10**) is more reactive than the isomer (**11**) in cycloaddition reactions,[7] but nucleophilic attack occurs very readily on both isomers[8] and they are known to equilibrate rapidly in the presence of fluoride ion.[9] Thus, reaction to yield compound (**17**) may occur *via* both or either of Paths A1 and A2. It appears, therefore, that when possible, the preferred mode of reaction of pyrocatechol is to form seven-membered rings but this does not occur with the perfluorocycloalkenes (**6**) and (**7**) where the products would be bridgehead alkenes.

Reaction of hexafluoropropene (**12**) with pyrocatechol gave two compounds, (**18**) and (**19**), obtained *via* addition rather than substitution processes; this may be attributed to the less electron-deficient nature of the double bond of the alkene (**12**). In an attempt to avoid addition reactions, the dilithio derivative of pyrocatechol was treated with hexafluoropropene and the heterocyclic derivatives (**20**) and (**21**) were obtained. Attempts to convert the spiroacetal (**14**) into perfluorocyclopent-2-enone were unsuccessful; compound (**14**) was stable to acid hydrolysis, even surviving 50% sulphuric acid at reflux. Compound (**14**) was also recovered unchanged after prolonged stirring with boron trifluoride–diethyl ether.[10]

We next turned our attention to reactions of toluene-3,4-dithiol (**2**) as a difunctional nucleophile. Reaction of (**2**) with the fluoro-alkene (**8**) gave an inseparable mixture of products, whereas perfluorocyclo-butene (**6**) and -pentene (**7**) gave *p*-dithiine derivatives (**22**) and (**23**), respectively, *via* Path B2 (see Scheme). It is clear, therefore, that the ability of sulphur to stabilise adjacent centres of negative charge favours cyclisation *via* the intermediate carbanion shown (Path B2, Scheme) in



Scheme. General possible reactions of F-alkene with difunctional nucleophile

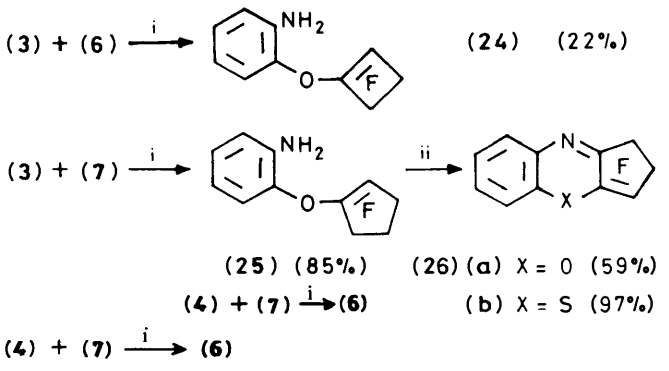


Reaction conditions: i, K_2CO_3, 20 °C, MeCN

Reaction conditions: i, K_2CO_3, 20 °C, MeCN; ii, MeCN, 20 °C

contrast to the di-oxygen nucleophiles which react *via* path B1, as described earlier. Krespan and England[11] have prepared similar cyclic sulphides from reactions of fluoro-olefins with sulphide ion.

Treatment of *o*-aminophenol (**3**) with perfluoro-cyclobutene (**6**) and with -cyclopentene (**7**) gave the unstable ethers (**24**) and (**25**) respectively. The lower reactivity of an amino group compared with an hydroxy group therefore enables the reaction to terminate subsequent to single vinylic displacement of fluoride ion.

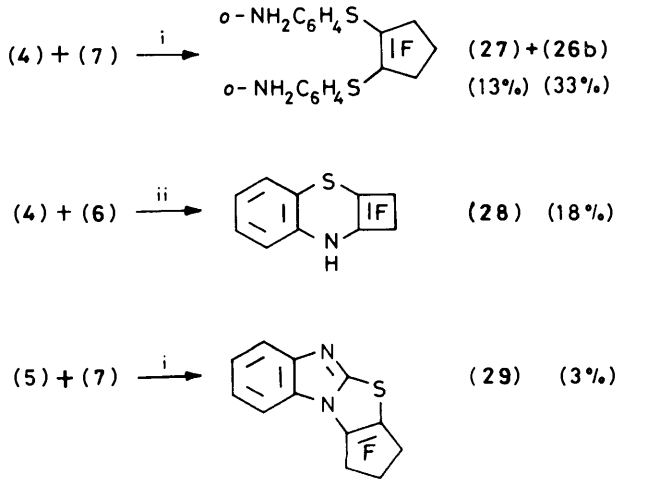


Reaction conditions: i, K_2CO_3, 20 °C, MeCN; ii, NEt_3, reflux, MeCN

However, further reaction of compound (**25**) with triethylamine in refluxing acetonitrile promoted loss of two molecular proportions of hydrogen fluoride and a product was isolated that was assigned structure (**26a**) on the basis of analytical and spectroscopic data (especially ^{19}F, ^{13}C, and ^{15}N n.m.r.). Under similar conditions compound (**24**) gave only intractable tars. The observation of compound (**26a**), formed through Path B2 (see Scheme), with subsequent 1,4-dehydrofluorination, contrasts with the proposed mechanism for the reaction of pyrocatechol (**1**) and it is probable, therefore, that (**26a**) is the product of thermodynamic control, *i.e.* Step B1 in this case is reversible.

When *o*-aminothiophenol (**4**) was treated with perfluoro-cyclopentene (**7**) compound (**26b**) was formed, analogous to the final product from *o*-aminophenol (**26a**). In the case of (**4**), however, no intermediate analogous to (**25**) was isolated and the failure to observe such an intermediate further demonstrates the activating influence of sulphur connected to an unsaturated site. Remarkably, when the same reaction was conducted for a shorter period the disulphide (**27**) was formed, *i.e.* involving displacement of two vinylic fluorines by ArS^- units. Compound (**27**) was not, however, converted into (**26b**) by simply stirring in acetonitrile with potassium carbonate. Consequently, fluoride generated in the formation of (**27**) must lead to a small equilibrium concentration of the analogue of (**25**), even though we have been unable to detect it, and (**26b**) is, therefore, formed from this intermediate providing that sufficient time is allowed for the process to occur. Perfluorocyclobutene (**6**) and *o*-aminophenol gave compound (**28**), *via* path B2 (Scheme). However, further loss of hydrogen fluoride to give the analogue of (**26b**) is obviously inhibited by ring strain.

The alkene (**8**) gave no tractable products on reaction with *o*-aminophenol (**3**) or *o*-aminothiophenol (**4**). Benzimidazolethiol (**5**) will also act as an ambident nucleophile,[12] but we obtained only a very low yield of product (**29**) with perfluorocyclopentene (**7**) and further reactions of (**5**) with our systems were not pursued.



Reaction conditions: i, K_2CO_3, 20 °C, MeCN; ii, NEt_3, −78 °C→20 °C, ether

Experimental

Details of instrumentation have been described previously.[3b] All n.m.r. spectra were obtained as solutions in $CDCl_3$ with external reference $CFCl_3$ for ^{19}F spectra, $SiMe_4$ for ^1H spectra, and $MeNO_2$ for ^{15}N spectra; i.r. spectra were recorded as neat liquids or as KBr discs as appropriate. When weights of products are not given, percentage yields quoted were measured by g.l.c. analysis using a gas-density balance detector.

Reaction of Pyrocatechol (**1**).—(a) *With perfluorocyclobutene* (**6**). A mixture of pyrocatechol (6.9 g, 63 mmol), and alkene (**6**) (10.2 g, 63 mmol), and potassium carbonate (11.0 g, 80 mmol) in acetonitrile (200 ml) was placed in a sealed tube and agitated at room temperature for 48 h. After filtration and removal of solvent the resultant oil (14 g) was shown by g.l.c. to comprise one major component which was isolated by preparative scale g.l.c. and identified as 2′,3′,4′,4′-*tetrafluorospiro*[1,3-*benzodioxole*-2,1′-*cyclobut*-2′-*ene*] (**13**) (67%) (Found: C, 51.5; H, 1.5; F, 33.2. $C_{10}H_4F_4O_2$ requires C, 51.7; H, 1.7; F, 32.7%); *m/z* 232 (M^+); $\nu_{max.}$ 1 785, 1 480, 1 230, 950, and 740 cm^{-1}; δ_F 120.8 (2 F, dd, *J* 18 and 8 Hz, CF_2) and 133.5 (2 F, overlapping multiplet, vinylic F); δ_H 6.7 (m, ArH).

(b) *With perfluorocyclopentene* (**7**). A mixture of pyrocatechol (8.0 g, 72 mmol), the alkene (**7**) (16.0 g, 75.5 mmol), and potassium carbonate (13.9 g, 100 mmol) in acetonitrile (200 ml) was sealed in a tube and agitated at room temperature for 24 h when filtration and evaporation left a yellow oil (19.3 g). Volatile material was transferred to a cold trap and found to be a single product identified as 2′,3′,4′,4′,5′,5′-*hexafluorospiro*[1,3-*benzodioxole*-2,1′-*cyclopent*-2′-*ene*] (**14**) (10.2 g, 50%) (Found: C, 46.8; H, 1.4; F, 40.1. $C_{11}H_4F_6O_2$ requires C, 46.8; H, 1.4; F, 40.4%); *m/z* 282 (M^+); $\nu_{max.}$ 1 758, 1 578, 1 380, 1 230, 990, 960, and 740 cm^{-1}; δ_F 128.9 (2 F, dd, both *J* 12 Hz, $=CCF_2$), 139.3 (2 F, dd, both *J* 5 Hz, $=CCF_2CF_2$), 159.5 (1 F, tt, *J* 12 and 5 Hz, $=CFCF_2$), and 165.0 (1 F, tt, *J* 12 and 5 Hz, $CFCCO_2$); δ_H 6.7 (m, ArH); δ_C 108.8 (d, *J* 159 Hz, ArC), 122.8 (d, 167 Hz, ArC), 137.0 (dt, *J* 294 and 25 Hz, $=CCF_2$), 139.3 (d, *J* 294 Hz, $C=CF_2$), 126.2 (m, spiro C), 145.6 (s, ArC) and 107—115 p.p.m. (unassigned).

(c) *With the alkene* (**8**). A mixture of pyrocatechol (2.95 g, 27 mmol), the alkene (**8**) (11.5 g, 29 mmol), and potassium carbonate (6.8 g, 49 mmol) in acetonitrile (70 ml) was stirred at room temperature for 84 h. Water (150 ml) was added and the lower layer was separated and transferred under reduced pressure to a cold trap and shown to be a mixture of three isomers by g.l.c.–m.s. (all *m/z* 470). The major component was purified by preparative scale g.l.c. and identified as 2-*pentafluoroethyl*-2,3,4-*tris*(*trifluoromethyl*)-2H-1,5-*benzodioxepine* (**15**) (49%) (Found: C, 36.2; H, 0.7. $C_{14}H_4F_{14}O_2$ requires C, 35.8; H,

0.9%); *m/z* 470 (M^+, 4%); $\nu_{max.}$ 1 612 and 1 230 cm^{-1}; δ_F 53.1 (3 F, m, CF_3CCF_2), 64.9 [3 F, qt, *J* 12 and 2 Hz, $CF_3C(C_2F_5)$], 69.3 (3 F, q, *J* 16 Hz, CF_3CO), 80.2 (3 F, s, CF_3CF_2), and 119.0 and 120.4 (2 F, AB, *J* 230 Hz, CF_2); δ_H 7.8 (m, ArH).

(d) *With alkene* (**9**). A mixture of pyrocatechol (2.8 g, 28 mmol), alkene (**9**) (14.0 g, 28 mmol), potassium carbonate (6.4 g, 47 mmol) and acetonitrile (70 ml) was stirred at room temperature for 144 h. Water (250 ml) was added and the lower layer that formed was separated, and volatile material was transferred under reduced pressure and then purified by preparative scale g.l.c. to yield 2,4-*difluoro*-3-(*perfluoro*-1-*ethyl*-1-*methylpropyl*)-2-*trifluoromethyl*-2H-1,5-*benzodioxepine* (**16**) (65%) (Found: C, 33.9; H, 0.4; F, 60.4. $C_{16}H_4F_{18}O_2$ requires C, 33.7; H, 0.7; F, 60.0%); *m/z* 570 (M^+); $\nu_{max.}$ 1 650br, 1 595, 1 322, 1 230, 1 066, 768, 743, and 730 cm^{-1}; δ_F 38.2 (1 H, br m, =CF), 55.3 (3 F, br s, $OCCF_3$), 76.2 (3 F, s, $=CCCF_3$), 77.8 (6 F, br s, CF_3CF_2), 101.4 (4 F, br s, CF_2), and 107.0 (CF, br s, OCF); δ_H 6.9 (m, ArH).

(e) *With the alkenes* (**10**) *and* (**11**). A mixture of pyrocatechol (1.7 g, 15.6 mmol), the alkenes (**10**) and (**11**) (*ca.* 1:1 mixture) (5.3 g, 16 mmol), and potassium carbonate (4.7 g, 34 mmol) was stirred in acetonitrile (120 ml) at room temperature for 72 h when the mixture was filtered, the solvent was removed, and the residue purified by transfer under reduced pressure into a cold trap to yield 1,1,2,2,2′,2′,3′,3′,4′,4′-*decafluoro*-1′,2′-*dihydrospiro*[*benzo*[b]*cyclobuta*[e]*dioxepine*-9,1′-*cyclobutane*] (**17**) (4.8 g, 75%) (Found: C, 42.9; H, 1.4; F, 47.7. $C_{14}H_4F_{10}O_2$ requires C, 42.7; H, 1.0; F, 48.2%); *m/z* 394 (M^+, 3%) and 294 ($M - C_2F_2$, 100%); $\nu_{max.}$ 1 700 and 1 220 cm^{-1}; δ_F 108.8 (2 F, br s), 118.6 (2 F, s), 122.0 and 130.8 (4 F, AB, *J* 224 Hz), and 129.2 and 139.2 (2 F, AB, *J* 215 Hz); δ_H 6.8 (m, ArH).

(g) *With hexafluoropropene* (**12**). A sealed tube containing a mixture of pyrocatechol (3.9 g, 35 mmol), the alkene (**12**) (5.0 g, 33 mmol), potassium carbonate (6.2 g, 45 mmol), and acetonitrile (50 ml) was agitated at room temperature for 24 h. Water was then added and the lower layer removed. Volatile material (6 g) was transferred under reduced pressure to a cold trap and shown by g.l.c. analysis to consist of two major components: compound (**18**) and compound (**19**) which were isolated by preparative scale g.l.c. o-(1,1,2,3,3,3-*hexafluoropropoxy*)*phenol* (**18**) (38%) (Found: C, 41.4; H, 2.6; F, 43.3. $C_9H_6F_6O_2$ requires C, 41.6; H, 2.3; F, 43.8%); *m/z* 260 (M^+); $\nu_{max.}$ 3 540, 3 420br, 1 600, 1 490, 1 380, 1 289, 1 189, 1 110, and 745 cm^{-1}; δ_F 75.1 (3 F, m, CF_3), 79.0 (2 F, m, CF_2), and 212.0 (CF, d, *J* 43 Hz, CFH); δ_H 4.3 (1 H, d, *J* 43 Hz, CFH), 5.3 (1 H, br s, OH), and 6.3 (4 H, br s, ArH). o-*Bis*(1,1,2,3,3,3-*hexafluoropropoxy*)*benzene* (**19**) (16%) (Found: C, 35.4; H, 1.3; F, 51.5. $C_{12}H_6F_{12}O_2$ requires C, 35.1; H, 1.5; F, 55.6%); *m/z* 410 (M^+), $\nu_{max.}$ 1 492, 1 381, 1 290, 1 200br, 1 120, and 745 cm^{-1}; δ_F 75.1 (3 F, m, CF_3), 79.0 (2 F, m, CF_2O), 212.0 (1 F, d, *J* 43 Hz, CFH); δ_H 4.3 (1 H, d, *J* 43 Hz, CFH) and 6.3 (4 H, br s, ArH).

The dilithio derivative of pyrocatechol was prepared by dropwise addition of butyl-lithium in hexane (1.6M; 42 ml, 67.2 mmol) to pyrocatechol (3.7 g, 33 mmol) in dry ether (150 ml) under nitrogen at −78 °C. The mixture was stirred for 1 h at −78 °C and then for 24 h at room temperature after which the solvent was evaporated to leave the dilithio derivative as a white solid. Acetonitrile (100 ml) was added to the solid and a gas reservoir containing hexafluoropropene (5.5 g, 36 mmol) was attached to the flask. The solution was stirred for 48 h at room temperature and then filtered and evaporated *in vacuo* to leave a product mixture which, purified by preparative scale g.l.c., gave the following. 2-*Fluoro*-2-(1,2,2,2-*tetrafluoroethyl*)-1,3-*benzodioxole* (**20**) (29%) (Found: C, 45.3; H, 2.85. $C_9H_5F_5O_2$ requires C, 45.02; H, 2.10%); *m/z* 240 (M^+); $\nu_{max.}$ 1 480, 1 289, 1 195, 900, and 738 cm^{-1}; δ_F 68.3 (1 F, m, *C*FCFH), 76.2 (3 F, ddd, *J* 11 and 6 Hz, CF_3), and 212.5 (1 F, ddq, J_{FH} 41, 19, and 11 Hz, CFH); δ_H 4.8 (1 H, dq, J_{FH} 41 and 6 Hz, CFH) and 6.6 (4 H, S, ArH). 2-*Perfluoroethylidene*-1,3-*benzodioxole* (**21**) (54%) (Found: C, 48.8; H, 2.15. $C_9H_4F_4O_2$ requires C, 49.11; H, 1.83%); *m/z* 220 (M^+); $\nu_{max.}$ 1 761, 1 476, 1 375, 1 228, 1 173, 1 120, 1 109, 998, and 740 cm^{-1}; δ_F 65.8 (3 F, d, *J* 16 Hz, CF_3) and 201.3 (1 F, q, *J* 16 Hz, CF); δ_H 6.8 (s, ArH).

Reactions of Toluene-3,4-*dithiol* (**2**).—(a) *With perfluorocyclobutene* (**6**). A sealed tube containing a mixture of toluene-3,4-dithiol (1.68 g, 10.8 mmol), the alkene (**6**) (2.0 g, 12.3 mmol), potassium carbonate (2.2 g, 16 mmol), and acetonitrile (150 ml) was agitated at room temperature for 24 h. The mixture was then diluted with water (150 ml) and extracted into ether; the extract was dried and evaporated to yield a solid (3.5 g), which was purified by sublimation *in vacuo* to afford 1,1,2,2-*tetrafluoro*-5-*methyl*-1,2-*dihydrobenzo*[b]*cyclobuta*[e]-p-*dithiine* (**22**) (2.4 g, 79%), m.p. 109—111 °C (Found: C, 47.2; H, 2.1; F, 27.7. $C_{11}H_6F_4S_2$ requires C, 47.5; H, 2.2; F, 27.3%); *m/z* 278 (M^+); $\nu_{max.}$ 1 310, 1 240, 1 100, 850, 810, and 600 cm^{-1}; δ_F 114.7 (s, CF_2); δ_H 6.8 (3 H, br s, ArH) and 2.2 (3 H, s, Me).

(b) *With perfluorocyclopentene* (**7**). A sealed tube charged with toluene-3,4-dithiol (3.1 g, 20 mmol), the alkene (**7**) (6.5 g, 30.7 mmol), potassium carbonate (4.8 g, 34.8 mmol), and acetonitrile (75 ml) was agitated at room temperature for 24 h. The crude mixture was then filtered and the solvent removed to leave a crystalline, yellow solid (6.0 g, 98%), m.p. 53—54 °C identified as 1,1,2,2,3,3-*hexafluoro*-6-*methyl*-2,3-*dihydro*-1H-*benzo*[b]-*cyclopenta*[e]-p-*dithiine* (**23**) (Found: C, 44.0; H, 1.6; F, 35.2. $C_{12}H_6F_6S_2$ requires C, 43.8; H, 1.8; F, 34.7%); *m/z* 328 (M^+); $\nu_{max.}$ 1 322, 1 270, 1 240, 1 098, 1 125, 1 000, 882, 850, and 816 cm^{-1}; δ_F 110.0 (4 F, s, $CF_2C=$) and 129.5 (2 F, s, $CF_2CF_2C=$); δ_H 7.1 (3 H, m, ArH) and 2.4 (3 H, s, Me).

Reactions of o-*Aminophenol* (**3**).—(a) *With perfluorocyclobutene* (**6**). A mixture of *o*-aminophenol (3.5 g, 32.1 mmol), the alkene (**6**) (4.8 g, 29.6 mmol), potassium carbonate (6.4 g, 47.1 mmol), and acetonitrile (200 ml) was sealed in a tube and agitated at room temperature for 24 h. Water was added and the lower layer (10.2 g) removed. Solvent was evaporated to leave a viscous oil (4.2 g) which on vacuum sublimation gave *o*-pentafluorocyclobut-1-enyloxyaniline (**24**) (1.6 g, 22%) (Found: C, 48.1; H, 2.4; N, 5.6. $C_{10}H_6F_5NO$ requires C, 47.8; H, 2.4; N, 5.6%); *m/z* 251 (M^+) $\nu_{max.}$ 3 460 and 3 280 (both NH_2), 1 755, 1 620, 1 370, 1 170, 1 000, and 750 cm^{-1}; δ_F 117.3 (2 F, d, *J* 7 Hz, CF_2CO), 119.3 (2 F, d, *J* 20 Hz, CF_2CF_2CO), and 134.2 (1 F, tt, *J* 20 and 7 Hz, =CF); δ_H 6.9 (4 H, br m, ArH) and 3.9 (2 H, s, NH_2).

(b) *With perfluorocyclopentene* (**7**). A sealed tube containing a mixture of *o*-aminophenol (2.8 g, 25.7 mmol), alkene (**7**) (5.5 g, 26 mmol), potassium carbonate (5.8 g, 42 mmol), and acetonitrile (200 ml) was agitated for 2.5 h at room temperature. Water was then added and the lower layer (11 g) separated. Residual solvent was evaporated and the remaining volatile material was transferred *in vacuo* to a cold trap and identified as o-*heptafluorocyclopent*-1-*enyloxyaniline* (**25**) (6.6 g, 85%) on the basis of comparison of i.r. and n.m.r. data with compound (**24**). Compound (**25**) $\nu_{max.}$ 3 450, 3 360 (both NH_2), 1 720, 1 620, 1 365, 1 175, 1 000, and 740 cm^{-1}; δ_F 116.8 (2 F, d, *J* 25 Hz, $CF_2C=$), 116.9 (2 F, s, CF_2CO), 131.1 (2 F, s, CF_2, CF_2CF_2) and 154.6 (1 F, m, CF); δ_H 6.6 (4 H, m, ArH) and 3.8 (2 H, s, NH_2). The sample rapidly decomposed at room temperature and mass spectral and analytical data could not be obtained.

Product (**25**) from the separate reaction of *o*-aminophenol (5.1 g, 46.7 mmol) and the alkene (**7**) (9.7 g, 45.8 mmol) carried out under conditions detailed above was refluxed with triethylamine (5 g, 49.5 mmol) in acetonitrile (200 ml) for 7 h. Water (300 ml) was then added and the product extracted with ether. The extract was dried ($MgSO_4$) and evaporated to leave a brown solid sublimation of which afforded *compound* (**26a**) as a

white solid, m.p. 103—103.5 °C (from CCl_4) [7.0 g, 59% based on the alkene (**7**)] (Found: C, 50.9; H, 1.2; N, 5.5; F, 36.0. $C_{11}H_4NF_5O$ requires C, 50.6; H, 1.2; N, 5.4; F, 36.4%); *m/z* 261 (M^+); $\nu_{max.}$ 1 705, 1 400, 1 350, 1 280, 1 110, 995, and 770 cm^{-1}; δ_F 117.8 (2 F, d, *J* 13 Hz, =CFCF_2), 124.3 (2 F, s, =CFCF_2CF_2), and 158.1 (1 F, t, *J* 13 Hz, =CF); δ_H 7.6 (br s, ArH); δ_C 151.3 (t, *J* 26 Hz), 143.6 and 135.9 (dt, *J* 298 and 26 Hz), 134.7, 131.5, 130.3, 126.2, and 116.0 (d, *J* 160 Hz), and 113 and 110 (both overlapping triplets, *J ca.* 260 Hz); δ_N −80.5 (=N).

Reactions of o-*Aminothiophenol* (**4**).—(a) *With perfluorocyclobutene* (**6**). A mixture of *o*-aminothiophenol (6.7 g, 53.6 mmol) and triethylamine (6.6 g, 65.3 mmol) in ether (100 ml) was cooled to −78 °C and connected to a gas bladder containing perfluorocyclobutene (12.4 g, 76 mmol). The mixture was stirred for 1 h at −78 °C and then for 8 h at room temperature. Ether was partially removed under reduced pressure and the residue was cooled to −15 °C. The solid product was collected, washed with water, and then sublimed *in vacuo* to give a green solid (2.4 g, 18%) identified as *compound* (**28**) (Found: C, 48.8; H, 2.0; N, 5.35. $C_{10}H_5SNF_4$ requires C, 48.58; H, 2.03; N, 5.66%); *m/z* 247 (M^+); $\nu_{max.}$ 3 410 (N–H), 1 675, 1 465, 1 430, 1 316, 1 282, 1 252, 1 205, 1 080, 980, 842, and 748 cm^{-1}; δ_F 110.9 (2 F, s, CF_2) and 117.4 (2 F, s, CF_2); δ_H 7.3—6.4 (4 H, m, ArH) and 5.4 (1 H, br s, NH).

(b) *With perfluorocyclopentene*. A mixture of *o*-aminothiophenol (2.8 g, 22.4 mmol), perfluorocyclopentene (4.6 g, 21.7 mmol), potassium carbonate (5.4 g, 39.1 mmol), and acetonitrile (145 ml) were sealed in a tube and agitated at room temperature for 1 h. Solids were filtered off and the filtrate was extracted with ether; the extract was dried and evaporated to yield a product, sublimination of which gave a yellow solid identified as *compound* (**27**) (1.0 g, 13%), m.p. 120 °C (Found: M^+, *m/z* 422.0261. $C_{17}H_{12}F_6N_2S_2$ requires M^+, 422.0348); $\nu_{max.}$ 3 361, 3 280 (both NH_2) 1 602, 1 248, 1 128, and 753 cm^{-1}; δ_F 108.0 (4 F, t, *J* 6 Hz) and 131.0 (2 F, p, *J* 6 Hz); δ_H 6.9 (8 H, m, ArH) and 4.1 (4 H, s, NH_2). When the reaction detailed above was carried out for 24 h the crude product (6.0 g, 97%) was shown to be a single component by n.m.r. spectroscopy and sublimation of a small portion yielded the *benzo*[b]*cyclopenta*[e]*thiazine* (**26b**), m.p. 120—121 °C (Found: C, 48.0; H, 1.6; F, 33.9; N, 5.3. $C_{11}H_4F_5NS$ requires C, 47.7; H, 1.5; F, 34.3; N, 5.1%); *m/z* 277 (M^+); δ_F 120.7 (2 F, d, *J* 14 Hz), 123.6 (2 F, s), and 137.3 (1 F, t, *J* 14 Hz); δ_H 7.1 (br m, ArH); $\nu_{max.}$ 1 624, 1 479, 1 342, 1 278, 1 111, 1 058, and 1 000 cm^{-1}. The compound decomposed with time in air at room temperature.

Reaction of Benzimidazole-2-thiol (**5**) *with Perfluorocyclopentene* (**7**).—A mixture of benzimidazole-2-thiol (**5**) (3.7 g, 24.7 mmol), perfluorocyclopentene (5.6 g, 26.4 mmol), and potassium carbonate (7.7 g, 55.8 mmol) in acetonitrile (200 ml) was stirred for 24 h at room temperature. Water (200 ml) was added and the product extracted with ether (2 × 200 ml). The extract was dried and evaporated to yield a solid (8 g) which upon sublimation afforded only a little solid (0.20 g) confirmed to be compound (**29**) (3%) (Found: M^+, *m/z* 322.0028. $C_{12}H_4F_6N_2S$ requires M^+, 322.0000]; δ_F 102.8 (2 F, s, CF_2), 109.7 (2 F, s, CF_2), and 124.0 (2 F, s, CF_2); δ_H 7.2 (br s, ArH).

References

1 Part 37, S. L. Bell, R. D. Chambers, R. Daniels, T. F. Holmes, and M. J. Silvester, *J. Fluorine Chem.*, submitted for publication.

2 (*a*) R. D. Chambers, 'Fluorine in Organic Chemistry,' Wiley, 1973, p. 148—170; (*b*) R. D. Chambers and R. H. Mobbs, *Adv. Fluorine Chem.*, 1965, **4**, 50 and references therein.

3 (*a*) S. Bartlett, R. D. Chambers, J. R. Kirk, A. A. Lindley, H. C. Fielding, and R. L. Powell, *J. Chem. Soc., Perkin Trans. 1*, 1983, 1235; (*b*) M. R. Bryce, R. D. Chambers, A. A. Lindley, and H. C. Fielding, *ibid.*, 1983, 2451; (*c*) R. D. Chambers, J. R. Kirk, and R. L. Powell, *ibid.*, 1983, 1239; (*d*) L. A. Rozov, N. S. Mirzabekyants, Yu. V. Zeifman, Yu. A. Cherburkov, and I. L. Knunyants, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1974, **23**, 1274.

4 (*a*) R. D. Chambers, A. A. Lindley, P. D. Philpot, H. C. Fielding, J. Hutchinson, and G. Whittaker, *J. Chem. Soc., Perkin Trans. 1*, 1979, 214; (*b*) R. D. Chambers, G. Taylor, and R. L. Powell, *J. Fluorine Chem.*, 1980, **16**, 161; (*c*) C. Camaggi and R. Stephens, *Tetrahedron Lett.*, 1966, **22**, 1189; (*d*) G. Gambaretto, M. Napolli, and S. Gliozzi, *Ann. Chim.*, 1969, **52**, 702 (*Chem. Abstr.*, **72**, 21382*c*); (*e*) R. G. Plevey and D. J. Sparrow, *J. Chem. Soc., Perkin Trans. 1*, 1976, 573; (*f*) R. G. Plevey and R. E. Talbot, *J. Fluorine Chem.*, 1977, **10**, 577; (*g*) D. Wojciech and H. Vollnagel-Neugebauer, *Bull. Pol. Acad. Sci., Chem.*, 1984, **32** (1—2), 39 (*Chem. Abstr.*, **102**, 6251d); (*h*) V. A. Doroginskii, A. F. Kolomiets, and G. A. Sokol'skii. *Zh. Org. Khim.*, 1983, **19** (8), 1762 (*Chem. Abstr.*, **99**, 212435q).

5 O. Scherer, H. Hahn, R. Hatwimmer, and S. Rebsdat, B.P. 1971, 12236491 (*Chem. Abstr.*, **75**, 49855v).

6 (*a*) D. C. England, L. R. Melby, M. A. Dietrich, and R. V. Lindsey, *J. Org. Chem.*, 1960, **82**, 5116; (*b*) M. Maruta, K. Kitazume, S. Kubota, N. Yoshimura, and N. Ishikawa, *Chem. Lett.*, 1979, 291.

7 A. E. Bayliff, M. R. Bryce, R. D. Chambers, J. R. Kirk, and G. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1985, 1191.

8 R. D. Chambers and G. Taylor, *J. Fluorine Chem.*, 1980, **16**, 161.

9 R. D. Chambers, G. Taylor, and R. L. Powell, *J. Chem. Soc., Perkin Trans. 1*, 1980, 429.

10 L. Alphonse and S. J. Arulray, *Indian J. Chem., Sect. B*, 1985, **24**, 199.

11 C. G. Krespan and D. C. England, *J. Org. Chem.*, 1968, **33**, 1850.

12 H. Alper and M. S. Wolin, *J. Org. Chem.*, 1975, **40**, 437; A. K. Bagrii, G. F. Galenko, and P. M. Kochergin, *Dopov. Akad. Nauk Ukr. RSR, Ser. B*, 1975, 801 (*Chem. Abstr.*, 1976, **84**, 43959w). For related reactions of imidazolethiol see M. R. Grimmett, E. T. van Horik, and S. R. Kulkarni, *Aust. J. Chem.*, in the press.

Received 24*th March* 1986; *Paper* 6/573