Tetrahedron. Vol. 27, pp. 669–680. Pergamon Press 1971. Printed in Great Britain

POLYFLUOROARYL ORGANOMETALLIC COMPOUNDS—XII[1]

NUCLEOPHILIC SUBSTITUTION IN OCTAFLUORODIBENZOTHIOPHEN, AND RELATED COMPOUNDS

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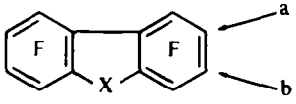
(*Received in the UK* 1 *September* 1970; *Accepted for publication* 13 *October* 1970)

Abstract— An unambiguous synthesis of heptafluoro-2-methoxydibenzothiophen (7) is reported. Structures for the products of substitution by MeO^- in octafluorodibenzothiophen (1), octafluorofluoren-9-one (3), and the related octafluoro-2,2′-dihydrobiphenyl (4) and ^{19}F NMR assignments are amended. Orientation of nucleophilic substitution in 2,2′-dibromooctafluorobiphenyl is established. The results of competition reactions for perfluorinated derivatives of the dibenzo series together with derivatives of the corresponding diphenyl systems are presented and discussed in relation to the orientation of nucleophilic substitution in these systems.

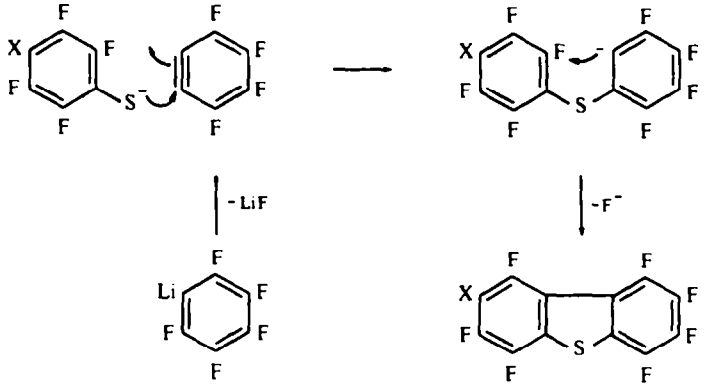
IN PREVIOUS papers[2–4] we have described the synthesis of and nucleophilic substitution in perfluoroaromatic derivatives of dibenzo series (1–3). We concluded from arguments



1: X = S
2: X = O
3: X = CO

based on NMR data that attack by methoxide ion occurred at (a) in octafluorodibenzothiophen (1), while attack at (b) occurred in octafluorodibenzofuran (2) and octafluorofluoren-9-one (3). However these results, and derived assignments i.e. for substitution in octafluoro-2,2′-dihydrobiphenyl (4), have become increasingly incompatible with results from a variety of independent work,[5] in particular Professor J. C. Tatlow has kindly brought to our notice unpublished results from his laboratory.

Recently we reported[1] a new synthesis of 1 starting from pentafluorothiophenol (5) and pentafluorophenyl-lithium and this process has now made possible a completely unambiguous synthesis of heptafluoro-2-methoxydibenzothiophen (7) shown in scheme I. Reaction of pentafluorobenzene with methoxide gives predominantly the *para*-substituted isomer[6] (8), which contained only two fluorine resonances in the ^{19}F NMR spectrum. This methyl ether (8) was converted to the thiol (9) by formation of the lithio derivative followed by reaction with sulphur.[7] Subsequent reaction of the derived thiolate anion (6) with tetrafluorobenzyne, which itself was generated by thermal decomposition of pentafluorophenyl-lithium, gave heptafluoro-2-methoxy-



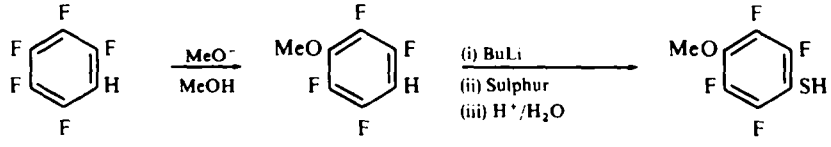
5: X = F
6: X = OMe

1: X = F
7: X = OMe

SCHEME 1

dibenzothiophen (7). This compound had both different spectral properties and m.p. from the OMe derivative obtained by reaction of methoxide ion with 1 and which had previously been assigned the structure 7.[2] Obviously the assignment must now be amended.

Substituent chemical shifts induced by the introduction of a OMe group into a polyfluoroaromatic system are well established (see later) and the original structure



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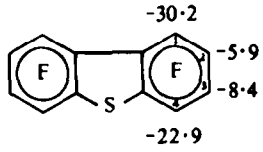
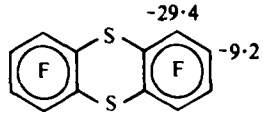
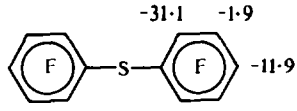
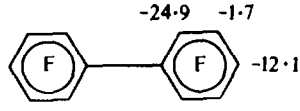
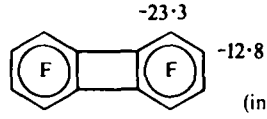
attributed to the product of attack by methoxide on 1 depended on a correct assignment of the two lowest field resonances in the ^{19}F NMR spectrum of 1.[2] From comparison with the very similar values of the chemical shifts of corresponding *ortho* F atoms in the model compounds 10–12 (see Table 1) the lowest field resonance at −30·2 ppm in 1 was originally assigned to the fluorine at the 4-position i.e. *ortho* to sulphur and the −22·9 ppm resonance to the 1-position, and this apparently received added confirmation from the biphenylene (13).[8] Nevertheless, these assignments must now be reversed on the basis of this new and unambiguous synthetic evidence, and the spectra are discussed in detail later in this paper.

Unfortunately the structures attributed to a number of other compounds depended on this earlier assignment of structure (see scheme II) since desulphurisation of 14 with Raney nickel yields 15 which was used to prepare a hexafluorodimethoxyfluoren-9-one (16) which, in turn, was found to be non-identical with a dimethoxy derivative

TABLE 1. SHIFTS (PPM) FROM C_6F_6, INTERNAL REFERENCE; SOLVENT ACETONE

1	
10	
11	
12	
13[a]	 (in C_6F_6)

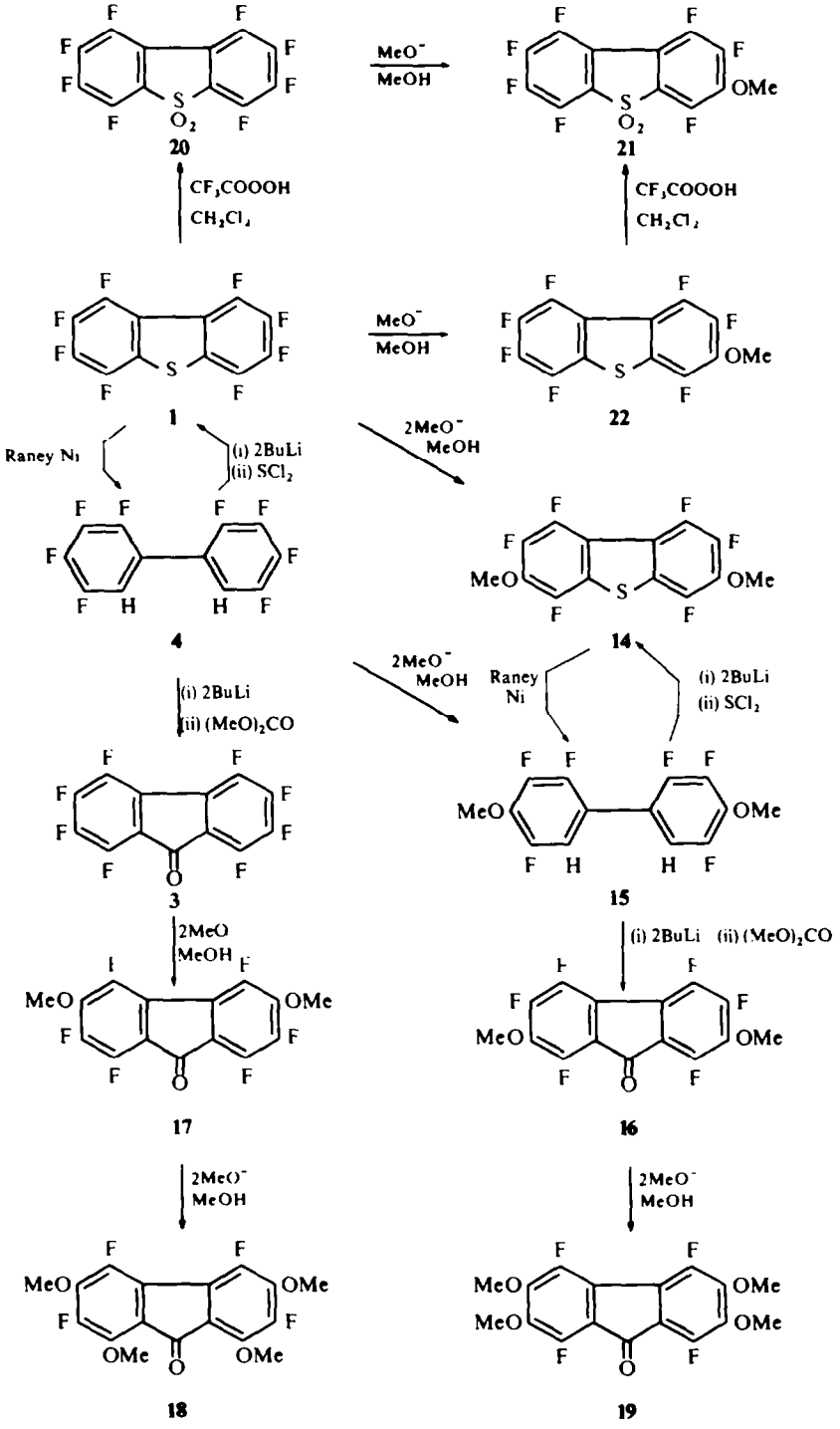
(**17**) obtained by reaction of **3** with two equivalents of methoxide ion.[4] Similarly nucleophilic substitution in octafluorodibenzothiophen-5,5-dioxide (**20**) by methoxide ion yielded principally heptafluoro-3-methoxydibenzothiophen-5,5-dioxide (**21**) which was also synthesised by oxidation of heptafluoro-3-methoxydibenzothiophen (**22**).[3]

The correct assignments are shown in scheme II, and the inter-relation of **14** and **15** has been confirmed by the conversion of **15** into **14** by the method indicated.

We have also prepared **14** and **16** from the dibromohexafluorodimethoxybiphenyl (**24**), made by the reaction shown in scheme III, and the NMR spectra of these compounds are entirely consistent with these structures and enable the orientation of nucleophilic substitution in **23** to be established.

In summary, the orientation of nucleophilic substitution in the biphenyls (**4**, **23** and **25**) is now clearly established as occurring initially at the 4 (and 4') positions and this is in accord with kinetics of substitution in the biphenyls and related polyfluoroaromatic systems.[5,9] With regard to the dibenzo derivatives (**1**–**3**), attack occurs *meta* to the hetero atom i.e. at b (see earlier) in octafluorodibenzothiophen as well as in octafluorodibenzofuran,[3] while attack occurs *para* to the carbonyl group (i.e. at a) in octafluorofluoren-9-one. There is an interesting correlation between these results and the order of reactivity of this group of dibenzo systems i.e. (**1**–**3**) together with

SCHEME II


MeO⁻ MeOH
CF₃COOH CH₂Cl₂
Raney Ni
(i) 2BuLi (ii) SCl₂
2MeO⁻ MeOH
(i) 2BuLi (ii) (MeO)₂CO
20
21
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22
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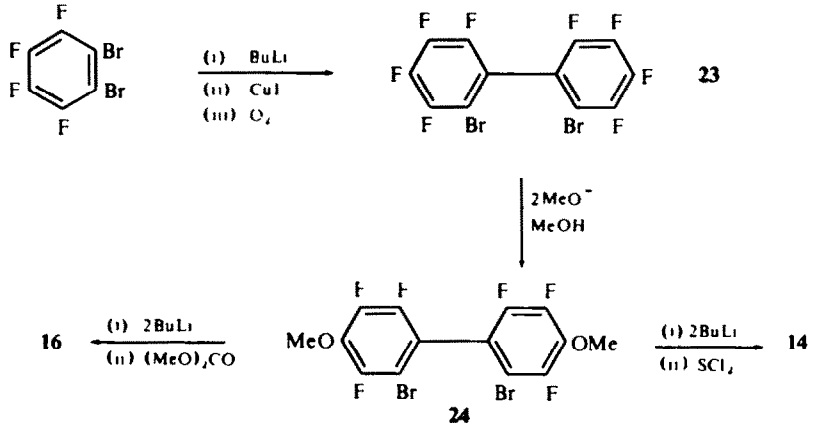
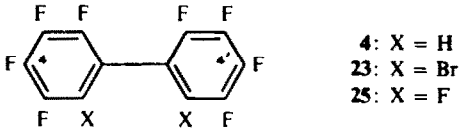
17
16
18
19

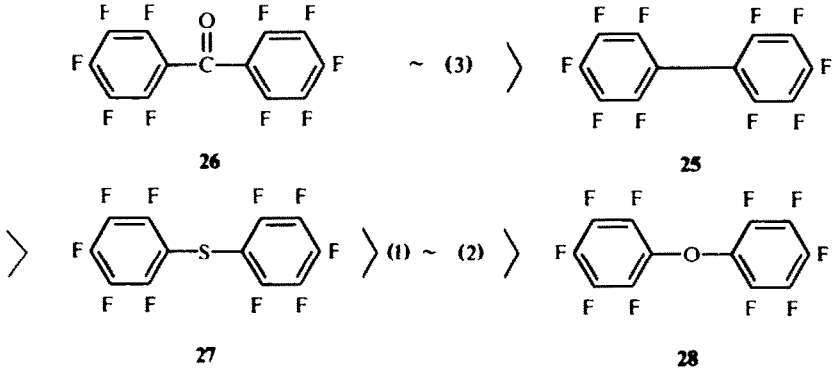


SCHEME III

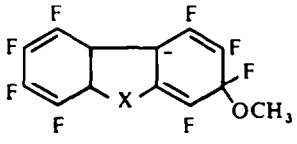


corresponding diphenyl derivatives. The order of reactivity shown below was obtained from a series of competition reactions for a deficiency of methoxide ion in methanol.

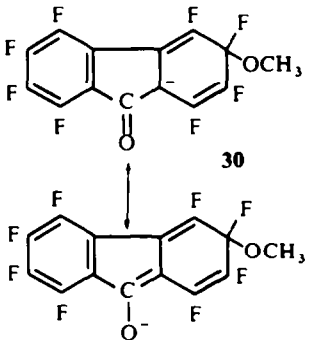
These results can be accommodated by a simple model assuming that substitution



occurs via Wheland Intermediates (**29** and **30**). The competition results indicate that the CO group, which is known to be very effective at stabilising an adjacent carbanionic centre,[10] is more able to direct orientation *para* to itself (**30**) than is a polyfluoroaromatic ring. The results also suggest that C_6F_5— is more efficient than C_6F_5S— in the same process and **29** is therefore preferred for octafluorodibenzothiophen. The low



29



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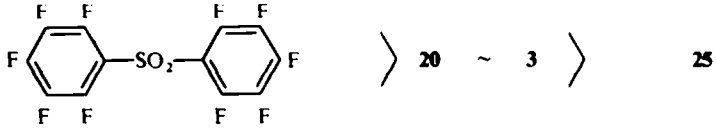
order of reactivity of **28** relative to **25** is in accord with this series and confirms our earlier discussion of the octafluorodibenzofuran system (**2**).[3]

However, octafluorodibenzothiophen-5,5-dioxide (**20**) also undergoes nucleophilic substitution in the 3-position by methoxide ion (i.e. b) and the simple model presented above cannot accommodate this result. Normally a sulphone group is at least as efficient as CO in stabilising an adjacent carbanionic centre[10] and this is indeed reflected in competition reactions because the reactivity order shown below has also been established.



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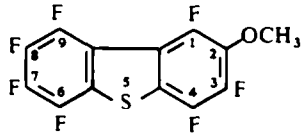
Similar substitution patterns for octafluorofluoren-9-one (**3**) and octafluorodibenzothiophen-5,5-dioxide (**20**), i.e. at a, would therefore be predicted by the simple model and, as yet, we have no explanation for the fact that a different pattern of substitution by methoxide ion in **3** and **20** is actually observed.

^{19}F *NMR spectra*

The chemical shifts and coupling constants for heptafluoro-2-methoxydibenzothiophen (**7**) are given in Table 2 and, as indicated earlier, the structure is established by unambiguous synthesis. Substituent chemical shifts for introducing OMe into a polyfluoroaromatic system usually fall into the following regions, *ortho* −4 to −6, *meta* +2, and *para* +2 ppm,[11] and by comparison of the shift values for **7** with those of the parent **1** the four absorptions attributed to the unsubstituted ring were selected on the basis of similarity with the values for **1**, and also allowing the OMe substituent shifts in **7** to be accounted for. Considering the remaining three resonances, the one at lowest field must be *ortho* to the methoxyl, having been shifted downfield from the value in **1**, and furthermore shows no *ortho* F—F coupling, which is normally in the range 18–22 Hz,[12] and consequently is assigned to F-1. Similarly, the only other fluorine resonance which can reasonably be regarded as being shifted downfield from the value in **1** is assigned to F-3, i.e. *ortho* to the methoxyl. The remaining resonance,

TABLE 2. ^{19}F NMR DATA FOR HEPTAFLUORO-2-METHOXYDIBENZOTHIOPHEN (ACETONE SOLUTION)

Shift (C_6F_6 internal reference)	*Fine structure* (Coupling constants in Hz)	*Assignments*
−36·9	D (J_{14} = 13·5) of D (J_{13} = 7·5)	1
−31·6	D (J_{98} = 18·0) of D (J_{96} = 13·2)	9
−23·1	D (J_{67} = 18·9) of D (J_{69} = 12·8)	6
−21·6	D (J_{43} = 19·4) of D (J_{41} = 13·6)	4
−14·2	Broad D (J_{34} ~ 19)	3
− 7·5	Broad T (J ~ 19)	7, 8
− 5·6	T (J ~ 18·0)	7, 8



for F-4, has been shifted upfield as anticipated for a fluorine *meta* to methoxyl. The values of the coupling constants confirm these assignments.

The assignment presented above clearly establishes that the lowest field resonance in the spectrum of **1** arises from F-1 and the next lowest field resonance from F-4 and this is the reverse of previous conclusions. As a cautionary note it is worth pointing out that the closely similar values of the model compounds (**10** to **13**) are in fact not applicable and that the shift for F-1 in **1** and the corresponding fluorines in **2** and **3**, and now **13**, are very variable in spite of an apparently similar environment, whereas in our original assignments they were constant to within ± 1 ppm. We can only suggest that inclusion of sulphur into the aromatic system in **1** makes invalid the use of **10** to **13** as models for **1**.

Reassignments of ^{19}F NMR spectra of compounds previously related to **1** by chemical means are included in Table 3.

TABLE 3

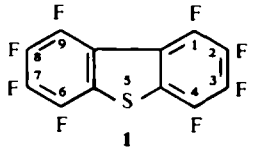
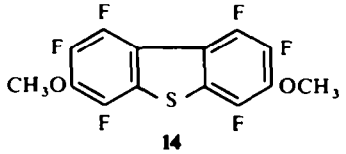
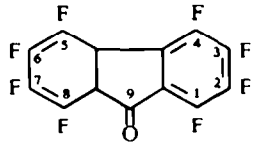
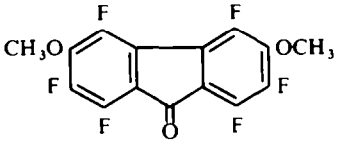
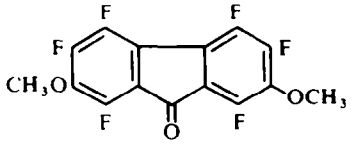
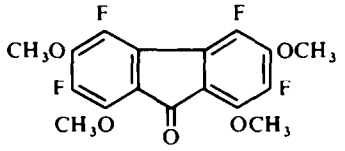
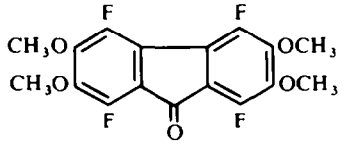
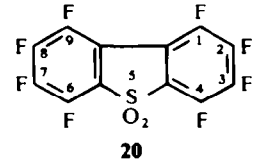
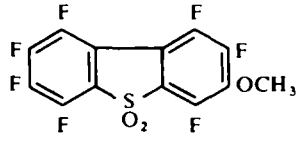
Compound	*Shifts* (ppm from C_6F_6 internal reference)		*Solvent*
 **1**	−30·2	F-1	acetone
	− 8·4	F-2	
	− 5·9	F-3	
	−22·9	F-4	
 **14**	−28·9	F-1	acetone
	−27·9	F-4	
	−10·4	F-2	

TABLE 3 (*cont.*)

Compound	*Shifts* (ppm from C_6F_6 internal reference)		*Solvent*
 **3**	−24·9	F-1	CH_2Cl_2
	−11·9	F-2	
	−19·6	F-3	
	−30·3	F-4	
 **17**	−22·1	F-1	CH_2Cl_2
	−13·3	F-2	
	−35·4	F-4	
 **16**	−29·8	F-1	CH_2Cl_2
	−22·6	F-3	
	−26·9	F-4	
 **18**	−18·4	F-2	CH_2Cl_2
	−32·8	F-4	
 **19**	−28·2	F-1	CH_2Cl_2
	−33·5	F-4	
 **20**	−35·0	F-1	acetone
	−19·5	F-2	
	−15·2	F-3	
	−22·4	F-4	
 **21**	−32·8 F-1,	−21·6 F-6	acetone
	−23·2 F-2,	−13·8 F-7	
	−27·3 F-4,	−18·8 F-8	
		−32·8 F-9	

EXPERIMENTAL

Unambiguous synthesis of heptafluoro-2-methoxydibenzothiophen (7)

(i) 2,3,5,6-*Tetrafluoroanisole* (8).[6] A soln of Na (2·3 g, 0·1 mole) in dry MeOH (50 ml) was added dropwise to a refluxing soln of pentafluorobenzene (16·8 g, 0·1 mole) in dry MeOH (60 ml). After refluxing for 17 hr the mixture was poured into dil H_2SO_4 and extracted with ether. The extracts were dried ($CaCl_2$) and the solvent distilled off to leave a residual oil which was then distilled (b.p. 138°/760 mm) to yield a colourless liquid (14·2 g, 79%) which on analytical GLC (silicone elastomer, 140°) showed only a single component. The ^{19}F NMR spectrum showed two equal resonances at −22·1 and −4·4 ppm from C_6F_6 (internal reference) and the ^1H NMR indicated two absorptions at 6·0 τ (CH_3 protons) and 3·0–3·7 τ (aromatic hydrogen).

(ii) *Tetrafluoro-4-methoxythiophenol* (9).[7] n-BuLi (34 ml of a hexane soln, 68 mmoles) was added dropwise to a stirred soln of tetrafluoro-4-methoxyanisole (11·5 g, 64 mmoles) in dry ether (100 ml) at −75°, contained in a 500 ml flask which had previously been baked in an oven overnight and purged with dry N_2. The mixture was stirred at −75° for 3 hr and at −60° for 2 hr; powdered S (2·0 g, 63 mmoles) was then added and the mixture allowed to warm to −45° over 45 min before hydrolysis with dil H_2SO_4. The organic layer was separated, the aqueous layer extracted with more ether, the extracts combined and dried ($CaCl_2$). The solvent was removed on a rotary evaporator and the residual oil fractionated under reduced pressure (6 mm) to yield starting material (4·3 g) (boiling range 40°–45°) and a product (5·6 g) boiling at 80°/6 mm (conversion 63%, yield 66%). Analytical scale GLC indicated the product to be a single component and its IR spectrum was identical with that of an authentic sample of 9.[7] The ^{19}F NMR showed two equal resonances at −23·5 and −4·9 ppm from C_6F_6 (internal reference).

(iii) *Cyclisation to* 7. n-BuLi (39 ml of a hexane soln, 93·4 mmoles) was added dropwise to a stirred soln of bromopentafluorobenzene (11·5 g, 46·6 mmoles) and tetrafluoro-4-methoxythiophenol (9·9 g, 46·7 mmoles) in dry ether (190 ml) at −75°, contained in a 500 ml flask which had previously been heated overnight in an oven and then purged with dry N_2. After 30 min the cooling bath was removed and the reaction mixture allowed to warm to room temp over 1 hr, and after 3 hr at room temp the mixture was refluxed for 18 hr. The mixture was then hydrolysed (dil H_2SO_4) and the separated organic layer was dried ($CaCl_2$). Removal of the solvent on a rotary evaporator left a yellow oil which was eluted down an alumina column (40°–60° light petroleum); a yellow band moved down the column leaving a dark band at the top. Evaporation of the solvent from the yellow fraction left a further yellow oil which on sublimation (~ 100°/10^{-2} mm) yielded a white solid (6·5 g). Analytical scale GLC (silicone elastomer, 220°) indicated that it consisted of two major components (in the approximate ratio 2:1 in order of increasing retention time) and several minor components. Also the component present in greatest amount appeared to have a retention time similar to previously prepared samples of heptafluoromethoxydibenzothiophen. This mixture was separated on preparative scale GLC (silicone elastomer, 200°) to yield *heptafluoro-2-methoxydibenzothiophen* 7 (~ 25%) (Found: C, 46·2; H, 0·94; F, 39·6. $C_{13}H_3F_7OS$ requires: C, 45·9; H, 0·9; F, 39·1%) m.p. 83°–84°. The mass spectrum shows strong peaks at *m/e* 340 (P^+), *m/e* 325 ($P^+ - CH_3$), *m/e* 297 ($P^+ - CH_3 - CO$) and metastables at 310·9 ($340^+ \rightarrow 325^+ + 15$, calc. value 310·7) and 272·0 ($325^+ \rightarrow 297^+ + 28$, calc. value 271·4).

Hexafluoro-2,2′-dihydro-4,4′-dimethoxybiphenyl (15)

(a) *From octafluoro-2,2′-dehydrobiphenyl.* A soln of Na (3·1 g, 135 mmoles) in dry MeOH (60 ml) was added dropwise to a refluxing soln of octafluoro-2,2′-dihydrobiphenyl (16 g, 54 mmoles) in dry MeOH (80 ml). Refluxing was continued for 72 hr and the mixture then poured into dil H_2SO_4 and extracted with ether. The extracts were dried ($CaCl_2$) and after removal of the solvent on a rotary evaporator the residue was sublimed (~ 110°/10^{-2} mm) to yield a white solid (16·1 g, 93%) which was shown by analytical scale GLC (silicone elastomer, 220°) to consist of a single component. Recrystallisation from hexane/$CHCl_3$ yielded white needles of *hexafluoro-2,2′-dihydro-4,4′-dimethoxybiphenyl* **15** (Found: C, 52·3; H, 2·59; F, 35·8. $C_{14}H_8F_6O_2$ requires: C, 52·2; H, 2·48; F, 35·4%) m.p. 125–126°. The ^{19}F NMR spectrum, in acetone soln, showed three resonances at −29·6, −21·3 and −11·6 ppm which are assigned to the 3(3′), 6(6′) and 5(5′) fluorines respectively.

(b) *From hexafluoro-3,7-dimethoxydibenzothiophen.* Hexafluoro-3,7-dimethoxydibenzothiophen (0·8 g) and Raney Ni (10 g) were heated under reflux in abs EtOH (30 ml) for 24 hr. On cooling the Raney Ni was filtered off and washed with ether. The solvent was removed from the combined filtrate and washings to leave a white solid (0·6 g) which was shown by analytical scale GLC (silicone elastomer, 200°) to be a single component. Recrystallisation from MeOH yielded white needles of hexafluoro-2,2′-dihydro-4,4′-dimethoxybiphenyl, m.p. 126·5–127·5° which was identical (IR, NMR, mixed m.p.) with the sample made by reaction of octafluoro-2,2′-dihydrobiphenyl with two equivalents of NaOMe.

Hexafluoro-3,7-dimethoxydibenzothiophen (**14**)

(a) *From hexafluoro-2,2'-dihydro-4,4'-dimethoxybiphenyl.* THF (60 ml, freshly distilled from LAH) and dry hexane (50 ml) were contained in a flask, which had previously been heated overnight in an oven, purged with dry N_2 and cooled to $-75°$. n-BuLi (23 ml of a hexane soln, 46 mmoles) in dry hexane (20 ml) was added dropwise, followed by dropwise addition of a soln of hexafluoro-2,2'-dihydro-4,4'-dimethoxybiphenyl (6·7 g, 20·8 mmoles) in THF (50 ml). The resulting soln was stirred at $-75°$ for 4 hr and freshly distilled sulphur dichloride (2·1 g, 20·8 mmoles) in THF (20 ml) was added, dropwise. After warming slowly (1½ hr) to room temp the mixture was hydrolysed (dil H_2SO_4), the organic phase separated and dried ($MgSO_4$). Removal of the solvent on a rotary evaporator left an oily residue which on sublimation ($120°/10^{-2}$ mm) yielded a yellow solid (4·2 g) and analytical scale GLC indicated that it consisted almost entirely of one component (~50% yield). Recrystallisation from aqueous acetone and then from hexane/$CHCl_3$ yielded *hexafluoro-3,7-dimethoxydibenzothiophen* **14** (Found: C, 47·9; H, 1·75; F, 32·6. $C_{14}F_6O_2S$ requires: C, 47·7; H, 1·7; F, 32·4%) as white needles, m.p. 157–159°.

(b) *From octafluorodibenzothiophen.* A soln of Na (0·297 g, 12·9 mmoles) in dry MeOH (25 ml) was added dropwise to a refluxing soln of octafluorodibenzothiophen (1·9 g, 5·8 mmoles) in dry MeOH (50 ml). Reflux was continued for 23 hr, during which time a heavy white ppt appeared and, after cooling, the ppt (1·2 g) was filtered off. Analytical scale glc (silicone elastomer, 220°) indicated that the ppt was a single component (work up of the filtrate yielded a solid (0·7 g) which appeared to be a mixture of starting material, mono- and dimethoxy derivatives). Recrystallisation from hexane/$CHCl_3$ yielded white needles of **14** m.p. 157–159° which was identical (IR, NMR, mixed m.p.) with the sample made by cyclisation of hexafluoro-2,2'-dihydro-4,4'-dimethoxybiphenyl.

(c) *From 2,2'-dibromohexafluoro-4,4'-dimethoxybiphenyl* (**24**). n-BuLi (4·5 ml of a hexane soln, 10·8 mmoles) in dry hexane (20 ml) was added dropwise to a stirred soln of **24** (2·5 g, 5·2 mmoles) in THF (freshly distilled from LAH, 90 ml) and dry hexane (40 ml) at $-75°$, contained in a flask which had previously been heated overnight in an oven and then purged with dry N_2. After 2 hr at $-78°$ a soln of sulphur dichloride (freshly distilled, 0·55 g, 5·3 mmoles) in THF (20 ml) was added dropwise and after a further 30 min at $-75°$ the mixture was warmed slowly to room temp and hydrolysed (dil H_2SO_4). The organic layer was separated and dried ($MgSO_4$). Removal of the solvent on a rotary evaporator left a yellow solid, which gave a white sublimate ($120°/10^{-2}$ mm) (0·8 g., 44%), leaving a black tar. Recrystallisation of the sublimate (hexane/chloroform) yielded **14** (Found: C, 47·9; H, 1·7. Calc. for $C_{14}H_6F_6O_2S$; C, 47·7; H, 1·7%) as white needles m.p. 155–157°. The IR spectrum was identical with those of the two previously prepared samples of this compound, as described in (a) and (b) above. The mixed m.p. was found to be 156–158°.

2,2'-Dibromo-octafluorobiphenyl. n-BuLi (30 ml of a hexane soln, 72 mmoles) was added dropwise to a stirred soln of 1,2-dibromotetrafluorobenzene (22·0 g, 71·4 mmoles) in dry ether (140 ml) at $-75°$, contained in a flask which had previously been heated overnight in an oven and then purged with dry N_2. After 2 hr cuprous iodide powder (13·6 g, 71·5 mmoles) was added[13] and stirring continued at $-75°$ for 8 hr, and when the mixture had warmed slowly (2 hr) to room temp it was stirred at that temp for a further 12 hr. Dry O_2 was then bubbled into the mixture which turned black at once and became warm. When the temp of the soln had returned to room temp (~1 hr) the mixture was hydrolysed (6N HCl). The dark organic layer was separated and the aqueous layer extracted with more ether. The extracts were combined and dried ($CaCl_2$); solvent was removed on a rotary evaporator to leave a black oil. This was transferred to an alumina column and eluted (40–60° light petroleum) until no more solid material emerged. Removal of the solvent from the eluant left a crystalline solid which appeared to be contaminated with iodine. The iodine was removed under vacuum at room temp and then the product was sublimed (~$90°/10^{-2}$ mm) to yield a white solid (8·4 g, 52%). Analytical scale GLC (silicon elastomer, 220°) indicated that it contained a single component. The ^{19}F NMR data is similar to that reported previously[14] and shows (in acetone soln) four resonances at −35·4, −28·6, −12·6 and −8·2 ppm which are assigned to the 3(3'), 6(6'), 4(4') and 5(5') fluorines respectively. Each of these resonances showed first order splitting and analysis yielded the following F—F coupling constants: J_{34} = 20·6. J_{36} = 9·6. J_{35} = 3·7. J_{45} = 19·2. J_{46} = 4·4. J_{56} = 21·2 Hz. Also a through-space coupling $J_{66'}$ = 1·6 Hz was observed.

2,2'-Dibromohexafluoro-4,4'-dimethoxybiphenyl. A soln of Na (0·7 g, 30 mmoles) in dry MeOH (40 ml) was added dropwise to a refluxing soln of 2,2'-dibromo-octafluorobiphenyl (6·4 g, 14 mmoles) in dry MeOH (60 ml), contained in a 250 ml flask which had previously been purged with dry N_2. After refluxing for 22 hr, the mixture was poured into dil H_2SO_4 and extracted several times with ether; the extracts were combined and dried ($CaCl_2$). Removal of the solvent on a rotary evaporator left an oil which would not solidify. Distilation (b.p. ~$150°/10^{-2}$ mm) yielded a colourless liquid (6·1 g, 91%) which solidified within 2 hr.

Analytical scale GLC (silicone elastomer, 220°) indicated that it consisted of a single component. The solid was recrystallised (MeOH/water) to yield *2,2'-dibromohexafluoro-4,4'-dimethoxybiphenyl* **24** (Found: C, 35·3; H, 1·28. $C_{14}H_6F_6Br_2O_2$ requires: C, 35·0; H, 1·25%) as white needles m.p. 73–74°. The mass spectrum shows a strong parent at *m/e* = 478, 480, 482, and peaks at 463, 465, 467 ($P^+ - CH_3$), and 435, 437, 439 ($P^+ - CH_3 - CO$). The ^{19}F NMR spectrum (in acetone soln) showed three resonances at −40·8, −27·4 and −15·6 ppm (from C_6F_6 internal reference) which are assigned to the 3(3'), 6(6') and 5(5') fluorines respectively. Analysis of the first order fine structure yielded three F—F coupling constants as follows: $J_{56} = 20·3$, $J_{36} = 9·6$, $J_{35} = 6·8$ Hz.

Hexafluoro-2,7-dimethoxyfluoren-9-one (**16**). A mixture of THF (freshly distilled, 70 ml) and hexane (40 ml) at −75° was contained in a flask which had previously been heated in an oven and then purged with dry N_2. n-BuLi (7 ml, 17 mmoles) in dry hexane (20 ml) was added dropwise followed by a soln of 2,2'-dibromohexafluoro-4,4'-dimethoxybiphenyl (4·1 g, 8·5 mmoles) in THF (30 ml). After 1½ hr at −75°, dimethylcarbonate (0·8 g, 8·9 mmoles) was added rapidly and after a further 30 min at −75° the mixture was allowed to warm to −20° before hydrolysis (dil H_2SO_4). The bright yellow organic layer was separated and dried ($MgSO_4$). Removal of the solvent on a rotary evaporator left an orange oil which on sublimation yielded a dark coloured solid. Recrystallisation from hexane (the method used previously[4]) yielded an orange crystalline solid, and sublimation again yielded *hexafluoro-2,7-dimethoxyfluoren-9-one* **16** (0·3 g, 10%) (Found: C, 52·0; H, 1·9; F, 32·5. $C_{15}H_6F_6O_3$ requires: C, 51·7; H, 1·7; F, 32·8%) m.p. 148–150°. The mass spectrum showed a parent peak at *m/e* = 348, and a strong peak at *m/e* = 333 ($P^+ - CH_3$).

The IR spectrum was identical with that from the dimethoxyhexafluorofluoren-9-one (m.p. 152–153°) prepared by cyclisation of dimethoxyhexafluoro-2,2'-dihydrobiphenyl but not **17** made by reaction of octafluorofluoren-9-one with two equivalents of NaOMe.

Reaction of octafluorodibenzothiophen-5,5-dioxide with sodium methoxide

A soln of Na (0·097 g, 4·2 mmoles) in dry MeOH (15 ml) was added dropwise to a refluxing soln of octafluorodibenzothiophen-5,5-dioxide (1·5 g, 4·2 mmoles) in dry MeOH (30 ml). After refluxing for 16 hr the mixture was poured into dil H_2SO_4, extracted with ether and the extracts dried ($CaCl_2$). Removal of the solvent on a rotary evaporator left a yellow oil (1·4 g) which from analytical scale gas chromatography appeared to consist of one major component (~70%) and some minor components. By means of column chromatography (on neutral silica gel, eluting with 1:1 $CHCl_3$: 40–60° light petroleum) and thick layer chromatography [on "Kieselgel" (after Stahl)] a fraction was obtained containing the main component sufficiently pure for identification as heptafluoro-3-methoxydibenzothiophen-5,5-dioxide by comparison of its ^{19}F NMR, IR spectra and R_f value with the same compound made by the oxidation of **14**.[3]

It is probable that the minor products of this reaction contained some of the heptafluoro-2-methoxydibenzothiophen-4,4-dioxide since attempts to prepare a dimethoxy derivative yielded, even after column chromatography, an inseparable mixture of several components apparently containing different dimethoxy derivatives (mass-spec) none of which could be identified with any degree of certainty from the ^{19}F NMR spectrum.

Competition reactions

The procedure was to dissolve equal amounts of the two substrates (~0·2 mmoles of each accurately weighed out) in dry MeOH and then to add to the refluxing soln ~0·1 mmoles of NaOMe (in MeOH). After 24 hr, ether was added, the mixture extracted with water, and the organic layer dried ($CaCl_2$). The solvent was removed by distillation and the residue dissolved in chloroform. A GLC standard (usually one of the other compounds in the study since their GLC retention times are not too different) was weighed out (~0·1 mmoles) and added to the soln which was then analysed on a Griffin and George, D.6. Gas Density Balance Chromatography. The analysis was based on unused substrate and relative rate constants given below were obtained from the measured peak areas by the method of Cadogan and Sadler.[15]

Compound	*Rate* (relative to (1) = 1·0)
31	15
3, 26, 20	7
25	3
27	1·6
1, 2	1·0
28	0·2

Acknowledgement—We thank Professor J. C. Tatlow and Dr. J. Burdon for helpful discussion and exchange of information.

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