Polyfluoroarenes. Part IX.¹ Decafluorotolan: Synthesis, Properties, and Use as an Organometallic Ligand

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Di-iodoacetylene and pentafluorophenylmagnesium bromide give decafluorotolan (C6F5.C:C.C6F5) in good yield. The triple bond in the tolan undergoes ready catalytic hydrogenation, addition of bromine, and oxidative cleavage, but is relatively unreactive towards hydration, iodination, and carbonylation. Decafluorotolan reacts with methoxide ion in the 4- and 4'-positions, and gives a good yield of tetrakispentafluorophenylthiophen when it is heated with sulphur. Reaction of the tolan with cobalt octacarbonyl yields a complex $Co_2(CO)_6(C_6F_5:C:C\cdot C_6F_5)$, shown by its chemical and spectroscopic properties to be similar in structure to its hvdrocarbon analogue; octafluoro-4,4'-dimethoxytolan behaves similarly. Tetrakispentafluorophenylcyclopentadienone (perfluorotetracyclone) is obtained when a solution of the cobalt carbonyl complex of decafluorotolan is heated. Reaction of decafluorotolan with iron penta- or dodeca-carbonyl yields a complex $Fe_2(CO)_6(C_6F_5 \cdot C \cdot C_6F_5)_2$, together with perfluorotetracyclone.

In the absence of a catalyst, reactions between 1-halogenoalkynes and Grignard compounds usually lead to metathesis,2-4 e.g.,3

However, condensation is normally catalysed by cobalt(II) or copper(I) chloride, and under these conditions high yields of substituted alkynes may often be obtained.3-5 The influence of the catalyst is not fully understood, although it seems likely that an organo-cobalt or -copper intermediate is involved. The formation of such an intermediate has been proposed as the first stage in the reaction between Grignard compounds and 1-halogenoalkenes in the presence of cobalt(II) chloride.⁵

Decafluorotolan (I) is formed in 56% yield by the cobalt-catalysed reaction of di-iodoacetylene with pentafluorophenylmagnesium bromide in ether at -20° :

$$2C_{6}F_{5}\cdot MgBr + C_{2}I_{2} \xrightarrow{C_{0}CI_{2}} C_{6}F_{5}\cdot C:C \cdot C_{6}F_{5} + 2MgBrI$$
(I)

Its spectroscopic properties are fully consistent with the proposed structure. Strong infrared absorption at 1506 and 1527 cm.⁻¹ is characteristic of the pentafluorophenyl group,⁶ and a number of bands attributed to C-F vibrations appear in the region 900-1350 cm.⁻¹. The absence of absorption in the region 2000-3000 cm.⁻¹ indicates the symmetrical substitution of the -CiCgroup.⁷ The ultraviolet spectrum is remarkably similar to that of tolan itself (Table 1), and the ¹⁹F n.m.r. spectrum (Table 2) has three multiplets of relative intensity 2:1:2, attributable to the ortho-, para-, and metafluorine atoms of two equivalent pentafluorophenyl groups. Mass spectrometry reveals a parent ion of mass 358, and ions derived from it by the loss of simple carbonfluorine fragments.

Addition, Cleavage, and Substitution Reactions.---The

 * Fluorine is attached only to the aromatic rings in all the compounds described in this Paper.

Chem., 1945, 10, 298.

rate of hydrogenation of decafluorotolan over Raney nickel at atmospheric pressure and room temperature falls off after the absorption of 1 mol. of hydrogen, but both the decafluoro-cis-stilbene (II) (69% yield) and the



decafluorobibenzyl (III) (12%) * are formed. Similar results are obtained under more vigorous conditions $(80^{\circ} \text{ and } 25 \text{ atm.})$. The comparatively low-intensity u.v. absorption of the stilbene confirms that the expected 8 cis-form is produced; decafluoro-trans-stilbene, synthesised independently from trans-1,2-di-iodoethylene and pentafluorophenylmagnesium bromide in the presence of cobalt(II) chloride, has a more intense spectrum which is almost identical in intensity and shape with that of *trans*-stilbene itself, although it is displaced to shorter wavelengths by about 10 m μ (Table 1). The ¹⁹F and ¹H n.m.r. spectra of the hydrogenation product (Table 2) show the absence of bands arising from the trans-isomer. Attempts to convert decafluoro-cis-stilbene into the trans-isomer by use of iodine or iron dodecacarbonyl⁹ were unsuccessful.

Treatment of decafluorotolan with bromine in acetic acid at room temperature gives the $\alpha\beta$ -dibromo-compound (IV) in 67% yield, whilst oxidation of the tolan with potassium permanganate in acetone under the same conditions yields pentafluorobenzoic acid (72%).

Decafluorotolan is unreactive towards 97% formic

⁵ M. S. Kharasch and C. F. Fuchs, J. Amer. Chem. Soc., 1943, **65**, 504.

⁶ J. M. Birchall and R. N. Haszeldine, J. Chem. Soc., 1961, 3719.

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 ² F. Moulin, *Helv. Chim. Acta*, 1951, **34**, 2416; H. H.
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 ³ M. S. Kharasch, F. L. Lambert, and W. H. Urry, *J. Org.*

⁴ H. H. Schlubach and V. Franzen, Annalen, 1951, 572, 116; H. K. Black, D. H. S. Horn, and B. C. L. Weedon, J. Chem. Soc., 1954, 1704.

 ⁷ L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1958, p. 59.
 ⁸ P. Rumpf and M. Gillois, Bull. Soc. chim. France, 1955, 22,

conditions.¹⁰ Decafluorotolan is similarly unreactive towards iodine or mercuric acetate in refluxing acetic acid, and fails to react with carbon monoxide in the presence of nickel carbonyl or iron pentacarbonyl at up to 220° and up to 180 atm.

carbon analogue which yields deoxybenzoin under similar spectra of this compound are consistent with the proposed structure, and the n.m.r. spectrum shows a single proton resonance band and two equal-intensity ¹⁹F resonance bands (Table 2). The presence of only two

Table	1	

Ultraviolet spectra					
Compound	Solvent *		λ_{max} (m μ) (log ₁₀ ϵ)		
Decafluorotolan	Н	229 sh (4.00)	251sh (4.09)	264 (4.32)	
Tolan ⁸	н	278 (4.49) 228sh (4.02) 278 (4.40)	283 sh (4.30) 262 (4.33) 280 (4.20)	$\begin{array}{c} 295 & (4 \cdot 39) \\ 271 \text{sh} & (4 \cdot 36) \\ 208 & (4 \cdot 4) \end{array}$	
Decafluoro- <i>cis</i> -stilbene	н	278(4.49) 263(4.04)	289 (4.30)	298 (4.41)	
Decafluoro-trans-stilbene	Н	216 (3.95) 307sh (4.17)	285 (4.50)	295 (4.50)	
cis-Stilbene a	E	224 (4.39)	280 (4.02)		
trans-Stilbene ^a	Е	225sh (4.19) 295.5 (4.46)	$228\cdot 5$ (4.21) $307\cdot 5$ (4.45)	237sh (4.05) 321sh (4.25)	
$\alpha\beta\text{-Dibromodecafluorostilbene}$	н	$226 \text{sh} (4 \cdot 28)$	262 sh (4.22)	281 (4.35)	
Octafluoro-4,4'-dimethoxytolan	Н	266 sh (4.20) 266 sh (4.20) 313 (4.46)	283sh (4·43)	297 (4.54)	
Tetrakispentafluorophenylthiophen	н	235(4.53)	267sh (4·29)		
Tetraphenylthiophen ^b	E	239(4.38)	263 (4.27)	314(4.18)	
Perfluorotetracyclone	С	245(3.98)	317 (3.94)	437 (3·07)	
	в		317 (3.99)	433(3.10)	
	E	248 (3.98)	318 (3.83)	436(3.52)	
Tetracyclone	D c	262 (4.48)	340 (3.83)	509 (3.15)	
	I d	$260 \ (4 \cdot 45)$	342 (3.82)	512 (3.11)	
Tetrakistrifluoromethylcyclopentadienone ¹⁷	CT		340 (2.54)		
	в		364sh	381 (3.10)	
	\mathbf{M}	240 (4.00)	274 sh	356 (3.74)	
Cobalt complex (X)	С	270sh (4·39)	370sh (3·67)	438 (3.32)	
Iron complex (XIV)	Н	425 (3.55)		. ,	
* $B = Benzene$ (= chloroform (T = carbon tetrachlo	rido D - d	liovan E – ethe	nol U - howand	I	

Benzene, C = chloroform, CT = carbon tetrachloride, D = dioxan, E = ethanol, H = hexane, I = Iso-octane, M = methanol.

^a R. N. Beale and E. M. F. Roe, J. Chem. Soc., 1953, 2755. ^b L. Fortina and G. Montaudo, Gazzetta, 1960, 90, 987. ^c E. D. Bergmann and Y. Hirshberg, Bull. Soc. chim. France, 1950, 1095. ^d V. F. D'Agostino, M. J. Dunn, A. E. Ehrlich, and E. I. Becker, J. Org. Chem., 1958, 23, 1539.

The pentafluorophenyl groups of decafluorotolan are sufficiently reactive towards methoxide ion for substitution to take place without attack at the triple bond.

TABLE 2

¹⁹F Nuclear magnetic resonance spectra

	Sol	Chemical shifts †			
Compound	vent *	ortho	para	meta	
Decafluorotolan	Α	60·6q (2)	75.4t (1)	86.6m (2)	
Decafluoro- <i>cis</i> -stil- bene ±	СТ	$64 \cdot 2\hat{q}(2)$	76·0t (1)	84·2m (2)	
Decafluoro-trans-stil- bene ‡	Т	66·0m (2)	78-9t (1)	87·1m (2)	
Octafluoro-4,4'-di- methoxytolan ‡	А	61·7m (1)		81·2m (1)	
Tetrakispentafluoro- phenylthiophen	Т	62·3m (2) 64·0m (2)	75∙0m (1) 75∙4m (1)	85·1m (4)	
Cobalt complex (X) Cobalt complex (XI)	CT CT	58.9q(2)' 61.3m(1)	74·9t (Ì)′	82·8m (2) 81·1m (1)	

* A = Acetone, CT = carbon tetrachloride, T = tetrahydrofuran. † In p.p.m. upfield from CF3 CO2H (external intensities given in parentheses. \ddagger Proton resonances; *cis*-stilbene, τ 3·1; *trans*-stilbene, τ 2·6; dimethoxy-compound, τ 5.7; cobalt complex (XI), τ 5.5.

Sodium hydroxide in methanol converts it into octafluoro-4,4'-dimethoxytolan (V); the i.r., u.v., and mass acid under reflux conditions, in contrast to its hydrogroups of magnetically dissimilar fluorine atoms excludes all substitution patterns except 4,4', whilst the single proton band confirms that the methoxyl groups are equivalently substituted. The acetylene (V) is further characterised by formation of the dibromide (VI) and by oxidation to 2,3,5,6-tetrafluoro-4-methoxybenzoic acid.

$$C_{6}F_{5} \cdot C_{6}^{*}C \cdot C_{6}F_{5} \xrightarrow{\mathsf{NaOMe}} p \cdot \mathsf{MeO} \cdot C_{6}F_{4} \cdot C_{6}^{*}C \cdot C_{6}F_{4} \cdot \mathsf{OMe} \cdot p \xrightarrow{\mathsf{Br}_{2}/\mathsf{HOAc}} (V)$$

$$p \cdot \mathsf{MeO} \cdot C_{6}F_{4} \cdot \mathsf{CBr} \cdot \mathsf{CBr} \cdot \mathsf{C}_{6}F_{4} \cdot \mathsf{OMe} \cdot p \xrightarrow{\mathsf{(NP)}} (V)$$

$$p \cdot \mathsf{MeO} \cdot C_{6}F_{4} \cdot \mathsf{CBr} \cdot \mathsf{CBr} \cdot \mathsf{C}_{6}F_{4} \cdot \mathsf{OMe} \cdot p \xrightarrow{\mathsf{(NP)}} (V)$$

The existence of the triple bond in the dimethoxycompound (V) is established by the formation of the cobalt complex Co₂(CO)₆[C₁₄F₈(OMe)₂] (XI) during the reaction with cobalt octacarbonyl (see below).

Predominant substitution by nucleophiles in the 4-position of pentafluorophenyl derivatives is a common feature of polyfluoroarene chemistry. In the case of decafluorotolan, the orientating influence of the pattern of five fluorine atoms 11 will be reinforced by additional

¹⁰ J. Jadot and S. Mullers, Bull. Soc. roy. Sci. Liège, 1960, 29,

^{203.} ¹¹ G. M. Brooke, J. Burdon, M. Stacey, and J. C. Tatlow, J. Chem. Soc., 1960, 1768.

mesomeric stabilisation of the intermediate (VII) as shown.



In connection with the degradation reactions of the iron complex $\operatorname{Fe}_2(\operatorname{CO})_6(\operatorname{C}_{14}\operatorname{F}_{10})_2$ (XIV) (see below), it was of interest to synthesise tetrakispentafluorophenyl-thiophen (IX). The hydrocarbon analogue has been prepared through the metal complex (VIII), prepared

in most organic solvents and yields deep red air-stable solutions. Its ¹⁹F n.m.r. spectrum (Table 2) has three sharply defined bands, indicating the diamagnetism of the complex and attributed to the ortho-, meta-, and para-fluorine atoms of the two equivalent pentafluorophenyl groups. The i.r. spectrum has six bands in the terminal carbonyl region (1900—2150 cm.⁻¹), but no absorption in the bridging region (1800—1900 cm.⁻¹); ¹⁴ the absorption pattern is closely similar to that of hexacarbonyl(tolan)dicobalt(0), but the carbonyl bands of the fluorocarbon complex are shifted to higher frequencies by some 20—30 cm.⁻¹ (Table 3).

TABLE 3

Characteristic infrared absorption bands *

Compound	Origin	Absorption bands (cm. ⁻¹)					
$Co_{\bullet}(CO)_{\bullet}C_{1\bullet}F_{10}(X)$	C=O †	2105s	2075vs	2060sh	2049vs	2039s	2000sh
#	C ₆ F ₅ (ring) C-F	1643w 990s	1516s	1495 vs			
$Co_2(CO)_6C_{14}H_{10}$ \ddagger (hexane)	C=O	2099m	2059s	2034s	2028s	2017m	
$Co_2(CO)_6[C_{14}F_8(OMe)_2]$ (XI)	C=O	2096vs	2062 vs	2037s			
	[C ₆ F ₄ (OMe)] (ring) C–F	1634w 994s	1497sh	1479vs			
$Co_{2}(CO)_{4}(PPh_{3})_{2}C_{14}F_{10}$ (XII)	C=O†	2041vs	$2000 \mathrm{sh}$	1992vs	$1975 \mathrm{sh}$	1965 sh	1953s
	C ₆ F ₅ (ring) C–F	$1630 \mathrm{vw}$ 985s	1512s	1482vs			
$Fe_{2}(CO)_{6}(C_{14}F_{10})_{2}$ (XIV)	C=0 †	2100s	2066 vs	2045 vs	2024 vs	2012vs	1969s
	C ₆ F ₅ (ring) C–F	1650m 991vs	1529vs	1497vs			
$Fe_2(CO)_6(C_{14}H_{10})_2$ (ref. 18)	C=O	2075s	2024s	1992vs	1976s	1927s	
* Mulls in Nujol and hexachlor	obutadiene unless other	wise stated.	† CaF ₂ op	otics. ‡ G.	Bor, Chem	. Ber., 1963	, 96 , 2644.

from nickel sulphide and tolan,¹² but the direct reaction between tolan and sulphur has not been reported. Attempts to prepare the fluorocarbon analogue of the complex (VIII) led to the formation of a 2% yield of a dark green nickel-containing solid, which was soluble in chloroform. This approach to the thiophen derivative (IX) was discarded in favour of the direct reaction shown.

$$2C_6F_5 \cdot C_6 \cdot C_6F_5 + S \xrightarrow{\text{benzene}}$$

2,3,4,5-tetrakispentafluorophenylthiophen (72%)
(IX)

The i.r. spectrum of tetrakispentafluorophenylthiophen shows the characteristic fluoroaromatic ring absorption ⁶ at 1490 (very strong) and 1653 cm.⁻¹ (medium), together with a very strong C-F band at 988 cm.⁻¹; strong bands at 873 and 1515 cm.⁻¹ probably arise from skeletal vibrations of the thiophen ring.¹³ The u.v. spectrum of the thiophen (IX) is similar to that of its hydrocarbon analogue (Table 1), and the ¹⁹F n.m.r. spectrum (Table 2) shows the presence of two magnetically different types of pentafluorophenyl ring.

Reactions with Metal Carbonyls.—Cobalt octacarbonyl reacts readily with decafluorotolan in benzene at room temperature; 2 mol. of carbon monoxide are evolved, and hexacarbonyl(decafluorotolan)dicobalt(0) (X) is produced as deep red crystals. The complex is soluble ¹² G. N. Schrauzer and V. Mayweg, J. Amer. Chem. Soc., 1962, **84**, 3221.

A similar complex, hexacarbonyl(octafluoro-4,4'-dimethoxytolan)dicobalt(0) (XI), is formed from the dimethoxyacetylene (V); the i.r. carbonyl frequencies of this complex lie between those of the fluorocarbon and hydrocarbon complexes.



Bromination of the fluorocarbon complex (X) in acetic acid leads to $\alpha\beta$ -dibromodecafluorostilbene (IV), whilst octafluoro-4,4'-dimethoxytolan (V) is produced by the action of sodium hydroxide in methanol. A solution of iodine in pyridine regenerates decafluorotolan from the complex (X). The chemical and spectroscopic evidence is thus in accord with the formulation of complex (X) as the structural analogue of hexacarbonyl-(tolan)dicobalt(0); this is known to have a structure

 A. R. Katritzky and A. J. Boulton, J. Chem. Soc., 1959, 3500; A. R. Katritzky, Quart. Rev., 1959, 13, 362.
 E. W. Abel, Quart. Rev., 1963, 17, 142. involving two Co(CO)₃ groups linked by an acetylene bridge.15

Triphenylphosphine reacts with the complex (X) with the evolution of 2 mol. of carbon monoxide, and the formation of deep purple tetracarbonyl(decafluorotolan)bis(triphenylphosphine)dicobalt(0) (XII). The infrared spectrum of this compound in the terminal carbonyl stretching region is complex (Table 3). However, the shoulders are extremely weak, and at least two of them are likely to be 13C satellite bands. The most symmetrical structure for this complex has C_{2v} symmetry, for which group theory predicts three infraredactive carbonvl stretching frequencies.

In contrast to the hydrocarbon analogue,¹⁶ the decafluorotolan derivative (X) will not react with carbon monoxide (250 atm. at 200° in benzene for 44 hr.; 94%recovery) or with 50% aqueous sulphuric acid in refluxing methanol (82% recovery after 4 hr.). When a solution of the complex (X) is heated in benzene at 180°, red crystals of tetrakispentafluorophenylcyclopentadienone (XIII) (perfluorotetracyclone) can be isolated in 50% yield. The mass spectrum of this compound shows a parent-ion peak of mass 744, and a strong peak at mass 716 due to the $[(C_6F_5)_4C_4]^+$ ion arises through ready elimination of carbon monoxide from the parent ion. The u.v. spectrum of the ketone (Table 1) is similar in intensity to that of the hydrocarbon analogue, but the bands are shifted considerably to lower wavelengths. This is probably the result of a reduction in the planarity of the molecule, brought about by the bigger pentafluorophenyl groups. Unlike that of tetrakistrifluoromethylcyclopentadienone,¹⁷ the u.v. absorption spectrum is not especially dependent upon the solvent, indicating the absence of molecular complexes in solution. The failure of the ketone (XIII) to form such complexes reflects the lower electron-withdrawing power and greater steric effect of the pentafluorophenyl group compared with those of the trifluoromethyl group.

The i.r. spectrum of perfluorotetracyclone shows strong absorption at 1730 and 1652 cm.⁻¹, attributable to the carbonyl group and the double bonds, respectively, although the 1652 cm.⁻¹ band probably contains contributions from the fluoroaromatic rings; ⁶ the corresponding C=O and C=C absorptions of the trifluoromethyl derivative ¹⁷ occur at 1761 and 1684 cm.⁻¹.

Like the trifluoromethyl analogue, the ketone (XIII) does not form a 2,4-dinitrophenylhydrazone. Attempts to synthesise perfluorotetracyclone from decafluorotolan and carbon monoxide in the presence of iron dodecacarbonyl or cobalt octacarbonyl were unsuccessful.

Decafluorotolan, like tolan itself,¹⁸ gives a variety of products with iron penta- or dodeca-carbonyl in yields depending on the reaction conditions and the iron carbonyl employed. The major product under all the conditions investigated was a yellow crystalline complex (45% yield from iron dodecacarbonyl at 140°), for which analytical data and molecular weight measurements give the formula $C_{34}F_{20}Fe_2O_6$.

Six terminal carbonyl absorptions are observed in the infrared spectrum of the complex; these are shifted to high frequencies relative to the corresponding hydrocarbon complex C₃₄H₂₀Fe₂O₆, which, however, exhibits only five such frequencies. A medium-intensity absorption at 1650 cm.⁻¹ may be due to an unco-ordinated C=C bond, but is more likely to be a C₆F₅ skeletal vibration.⁶ The solubility of the complex is insufficient to permit the recording of a useful ¹⁹F n.m.r. spectrum, although the weak lines obtained are quite sharp, indicating the diamagnetism of the complex. At least six lines can be observed, which suggests the presence of two structurally different pentafluorophenyl groups.

The susceptibility of the polyfluoroarene ring to nucleophilic attack necessitates a careful choice of reagents for degradation reactions of the complex. Oxidation of the complex with bromine leads to moderate yields of the cyclic ketone (XIII), but none of the dibromo-compound (IV) could be isolated. Irradiation of a solution of the complex in benzene in the presence of sulphur gives a low yield of tetrakispentafluorophenylthiophen. The chemical evidence implies that the decafluorotolan fragment no longer exists as such in the complex, whilst both chemical and physical data suggest an unsymmetrical structure. The structure tentatively formulated (XIV) is of the type proposed for the complex formed from tolan itself.^{18,19} Minor products from the re-



actions of the iron carbonyls with decafluorotolan include the cyclic ketone (XIII).

EXPERIMENTAL

Infrared and u.v. spectra were measured with a Perkin-Elmer model 21 spectrophotometer (sodium chloride and calcium fluoride optics) and an Optica CF4 DR grating spectrophotometer, respectively. ¹⁹F and ¹H n.m.r. spectra were obtained with a Perkin-Elmer R10 spectrometer operating at 56.46 and 60.0 Mc./sec., respectively, chemical shifts being determined by the standard techniques with tri-

¹⁸ W. Hübel and E. H. Braye, J. Inorg. Nuclear Chem., 1959, 10, 250. ¹⁹ G. N. Schrauzer, J. Amer. Chem. Soc., 1959, 81, 5307.

 ¹⁵ W. G. Sly, J. Amer. Chem. Soc., 1959, **81**, 18.
 ¹⁶ U. Krüerke and W. Hübel, Chem. Ber., 1961, **94**, 2829.

¹⁷ R. S. Dickson and G. Wilkinson, J. Chem. Soc., 1964, 2699.

fluoroacetic acid or tetramethylsilane as external references. Mass spectra were obtained with an A.E.I. MS/2H instrument of resolution 1 in 700.

All operations involving the use of Grignard reagents were carried out under nitrogen.

Decafluorotolan.-Cobalt(II) chloride (dried in vacuo at 150°) (0.93 g., 7.2 mmoles) was added to a cooled (-20°) solution of pentafluorophenylmagnesium bromide [prepared from bromopentafluorobenzene (24.7 g., 100 mmoles) and magnesium (2.46 g., 101 mg.-atoms) in anhydrous ether (200 ml.)]. The mixture was stirred vigorously, and diiodoacetylene (13.9 g., 50.0 mmoles) in anhydrous ether (100 ml.) was added dropwise. The temperature was maintained at $-20^{\circ} \pm 5^{\circ}$ throughout the addition (30 min.) and for a further 2 hr., after which time the mixture was allowed to warm to room temperature. The mixture was acidified with aqueous 20% acetic acid, washed with water $(4 \times 100 \text{ ml.})$, dried (MgSO₄), and evaporated in vacuo at room temperature, to give a dark brown solid which crystallised from light petroleum (b. p. 60-80°) as platelets of decafluorotolan (10.1 g., 56%) (Found: C, 46.6; F, 52.3. C₁₄F₁₆ requires C, 46.9; F, 53.1%), m. p. 123-123.5°. The mass spectrum shows the following main peaks [m/e](rel. int.) (probable identity, P = parent)]: 358 (100) $(P)^+$; 289 (20) $(P - CF_3)^+$; 179 (8) $[(P)^{2+}$ or $(C_7F_{10})^+]$; 258 (8) $(P - C_2 F_4)^+$.

Hydrogenation of Decafluorotolan.—(a) At 1 atmosphere. A suspension of decafluorotolan (3.65 g., 10.2 mmoles) in ethanol (100 ml.) containing Raney nickel (0.5 g.) was hydrogenated at 1 atm. in a standard hydrogenation apparatus until 10.1 mmoles of hydrogen had been absorbed. Filtration of the reaction mixture followed by evaporation of the filtrate yielded a white waxy solid, which was recrystallised from ethanol and shown by n.m.r. spectroscopy to be a mixture of decafluoro-cis-stilbene (2.53 g., 69%) and decafluorobibenzyl (0.45 g., 12%). Repeated recrystallisation from light petroleum (b. p. 40—60°) gave pure 2,2',3,3',4,4',5,5',6,6'-decafluoro-cis-stilbene [Found: C, 46.5; H, $0.70'_{0}$; M (mass spectrum), 360. C₁₄H₂F₁₀ requires C, 46.7; H, $0.60'_{0}$; M, 360], m. p. 53°, subliming at 35—40° (bath).

(b) At 25 atmospheres. Decafluorotolan (0.51 g., 1.42 mmoles) was heated with methanol (8 ml.), Raney nickel (0.15 g.), and hydrogen (25 atm.) in a 16-ml. autoclave at 80° for 22 hr. The products were repeatedly recrystallised from light petroleum (b. p. 40–60°), and identified by i.r. and n.m.r. spectroscopy as pure decafluorobibenzyl (0.07 g., 15°_{0}) (plates; the less soluble component), m. p. and mixed m. p. 107–108° (lit.,⁶ 107–108°), and a mixture (0.37 g.) of decafluoro-*cis*-stilbene and decafluorobibenzyl, m. p. 47–53°.

Decafluoro-trans-stilbene.—Cobalt(II) chloride (3.00 g., 23.1 mmoles) was added to a cooled (-20°) solution of pentafluorophenylmagnesium bromide [prepared from bromopentafluorobenzene (16.8 g., 68.0 mmoles) and magnesium (1.70 g., 70.0 mg.-atoms) in ether (100 ml.)]. trans-1,2-Di-iodoethylene (6.20 g., 22.1 mmoles) 20 in ether (75 ml.) was added during 20 min. with vigorous stirring, and stirring was then continued while the mixture was allowed to attain room temperature. The mixture was hydrolysed with dilute aqueous acetic acid, washed with aqueous sodium hydrogen carbonate and water, dried (MgSO₄), and evaporated. The residue was sublimed *in vacuo*, to give di-iodoethylene (3.28 g., 53%), subliming at room temperature, and 2,2',3,3',4,4',5,5',6,6' decafluoro-trans-stilbene (0.94 g., 25% based on CHI:CHI consumed) [Found: C, 46.5; H, 0.8%; M (mass spectrum), 360. C₁₄H₂F₁₀ requires C, 46.7; H, 0.6%; M, 360], m. p. 96.5—97.5°, subliming at 80—90° (bath).

 $\alpha\beta$ -Dibromodecafluorostilbene.—A solution of decafluorotolan (0.64 g., 1.79 mmoles) and bromine (1.2 ml.) in glacial acetic acid (50 ml.) was shaken at room temperature for 20 hr. Water (50 ml.) and sodium pyrosulphite (2 g.) were then added, and the precipitated solid was filtered off, washed with water, dried *in vacuo* (P₄O₁₀), and sublimed at 80°/0.1 mm. on to a probe cooled to -78°. The white sublimate was $\alpha\beta$ -dibromodecafluorostilbene (0.62 g., 67%) [Found: C, 32.2; Br, 31.0%; *M* (vapour pressure osmometer in acetone), 505. C₁₄Br₂F₁₀ requires C, 32.4; Br, 30.99%; *M*, 518], m. p. 106°.

Oxidation of Decafluorotolan.—Decafluorotolan (0.52 g., 1.45 mmoles) was oxidised at room temperature with potassium permanganate (0.91 g., 5.7 mmoles) in anhydrous acetone (100 ml.). Water (100 ml.) was added, and the excess of permanganate was destroyed with sulphur dioxide. Acetone was removed ($50^{\circ}/15$ mm.) and the residual solution was acidified with 4N-sulphuric acid (20 ml.), and extracted with ether (4×50 ml.). The extracts were dried (MgSO₄) and evaporated; sublimation of the residue *in* vacuo at 60° yielded pentafluorobenzoic acid (0.44 g., 72°_{0}), m. p. and mixed m. p. $103-103\cdot 5^{\circ}$ (lit.,²¹ $103-104^{\circ}$), identified by i.r. spectroscopy.

Octafluoro-4,4'-dimethoxytolan.—Sodium hydroxide (0.50 g., 12.5 mmoles) was added to a suspension of decafluorotolan (1.07 g., 3.00 mmoles) in methanol (100 ml.), and the mixture was shaken for 6 hr. After about 15 min., the mixture became warm and the acetylene dissolved. A white crystalline precipitate appeared after about 1 hr., and at the end of the reaction this was filtered off and recrystallised from light petroleum (b. p. 60—80°), to yield 2,2',3,3',5,5',6,6'-octafluoro-4,4'-dimethoxytolan (0.95 g., 83%) [Found: C, 50.0; H, 1.8; F, 39.6%; M (mass spectrum), 382. $C_{16}H_6F_8O_2$ requires C, 50.3; H, 1.6; F, 39.8%; M, 382), m. p. 151—151.5°.

2,3,5,6-Tetrafluoro-4-methoxybenzoic Acid.—Octafluoro-4,4'-dimethoxytolan (0.38 g., 1.00 mmole), in anhydrous acetone (25 ml.), was oxidised with potassium permanganate (0.47 g., 2.90 mmoles) at room temperature. The mixture was worked up as in the oxidation of decafluorotolan, to yield the *product* (0.30 g., 67%) (Found: C, 42.8; H, 1.9%; Equiv., 224. $C_8H_4F_4O_3$ requires C, 42.9; H, 1.8%; Equiv., 224), m. p. 118—118.5°.

 $\alpha\beta$ -Dibromo-octafluoro-4,4'-dimethoxystilbene. Octafluoro-4,4'-dimethoxytolan (1.03 g., 2.70 mmoles), in glacial acetic acid (20 ml.), was heated under reflux (30 min.) with bromine (2.0 ml.). Water (25 ml.) was added to the cooled solution, and the precipitated solid was washed, dried, and recrystallised from light petroleum (b. p. 60—80°), to yield $\alpha\beta$ -dibromo-2,2',3,3',5,5',6,6'-octafluoro-4,4'-dimethoxystilbene (1.30 g., 89%) (Found: C, 35.5; H, 1.1; Br, 29.6. C₁₆H₆Br₂F₈O₂ requires C, 35.4; H, 1.1; Br, 29.5%), m. p. 142°.

Tetrakispentafluorophenylthiophen.—Decafluorotolan (2·45 g., 6·84 mmoles) and sulphur (0·58 g., 0·18 g.-atom) in anhydrous benzene (25 ml.) were heated in a sealed tube at 190° for 14 hr. The yellow solid recovered from the solution was recrystallised from light petroleum (b. p.

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²⁰ A. C. Pappas, Acta Chem. Scand., 1948, 2, 292.

²¹ E. Nield, R. Stephens, and J. C. Tatlow, J. Chem. Soc., 1959, 166.

100—120°) and sublimed *in vacuo* at 140°, to yield crystals of the *product* (1.84 g., 72%) [Found: C, 44.8; S, 4.6; F, 51.1%; M (mass spectrum), 748. $C_{28}F_{20}S$ requires C, 44.9; S, 4.3; F, 50.8%; M, 748], m. p. 180—180.5°.

Hexacarbonyl(decafluorotolan)dicobalt(0).—A solution of decafluorotolan (5.87 g., 15.6 mmoles) in anhydrous benzene (40 ml.) was added to a stirred solution of dicobalt octacarbonyl (5.56 g., 16.2 mmoles) in benzene (40 ml.) under nitrogen. The mixture was stirred (3 hr.) at room temperature until the evolution of gas had ceased (32.3 mmoles of CO evolved), and then evaporated. The residue was recrystallised from light petroleum (b. p. 60—80°) to yield deep red crystals of the *product* (9.24 g., 88%) (Found: C, 37.1; Co, 18.1. $C_{20}Co_2F_{10}O_6$ requires C, 37.2; Co, 18.3%), m. p. 99—101° (decomp.).

Hexacarbonyl(octafluoro-4,4'-dimethoxytolan)dicobalt(0). — Octafluoro-4,4'-dimethoxytolan (0·39 g., 1·02 mmoles), dicobalt octacarbonyl (0·34 g., 1·02 mmoles), and dry benzene (25 ml.) were shaken at room temperature until the evolution of carbon monoxide (2·11 mmoles) ceased (2 hr.). The solution was filtered, and the filtrate was evaporated (40°/15 mm.), to leave a dark purple residue (0·64 g., 97%), which was recrystallised from light petroleum (b. p. 30—40°) at -78° to give hexacarbonyl-(2,2',3,3',5,5',6,6'-octafluoro-4,4'-dimethoxytolan)dicobalt(0) [Found: C, 39·7; H, 0·9%; M (vapour pressure osmometer, in CHCl₃), 661. C₂₂H₆Co₂F₈O₈ requires C, 39·6; H, 0·9%; M, 668], m. p. 191° (decomp.).

Reactions of Hexacarbonyl(decafluorotolan)dicobalt(0).----(a) With bromine. When bromine (4.70 g., 29.3 mmoles) was added to a solution of the complex (0.65 g., 1.00 mmole) in glacial acetic acid (40 ml.), a rapid evolution of gas occurred and the colour of the solution changed from red to dark red-brown. The solution was shaken at room temperature for 20 hr., after which it was dark green; addition of water (40 ml.) then produced an orange colour and a solid precipitate. After treatment with aqueous sodium pyrosulphite, the mixture was filtered, and the residue was washed with water and dried *in vacuo* (P₄O₁₀). Vacuumsublimation at 100° gave white crystals of $\alpha\beta$ -dibromodecafluorostilbene (0.46 g., 89%), m. p. 106-107°, identified by infrared spectroscopy.

(b) With iodine. The complex (1.25 g., 1.94 mmoles) was stirred for 18 hr. at 40° with iodine (0.80 g., 3.1 mmoles) in pyridine (25 ml.). Carbon monoxide (9.2 mmoles) was evolved. Filtration of the reaction mixture yielded a residue of bispyridinecobalt(II) iodide (1.10 g., 70%), identified by i.r. spectroscopy; evaporation of the filtrate gave a further residue, which was sublimed *in vacuo* at 60° on to a probe cooled to -78° , to give decafluorotolan (0.45 g., 69°_{0}), m. p. 122°, identified by i.r. spectroscopy.

(c) With methoxide ion. The complex (0.495 g., 0.77 mmole), sodium hydroxide pellets (1.50 g., 0.037 mole), and methanol (80 ml.) were shaken together at room temperature for 20 hr. The initial red colour of the mixture disappeared after ca. 2 hr. and a white crystalline precipitate formed. Water (50 ml.) was added to the mixture, which was then filtered. Extraction of the residue with hot benzene, evaporation of the extracts, and recrystallisation of the residue from 1:1 benzene-light petroleum (b. p. 60-80°) yielded needles of octafluoro-4,4'-dimethoxytolan (0.195 g., 66%), m. p. 154-154.5°, identified by i.r. spectroscopy.

(d) With triphenylphosphine. The complex (0.49 g., 0.75 mmole), triphenylphosphine (0.39 g., 1.5 mmoles),

and anhydrous benzene (50 ml.) were heated under reflux for 2 hr. Carbon monoxide (1.5 mmoles) was evolved. The dark red solution was evaporated and the residue was recrystallised from benzene, to give deep purple crystals of *tetracarbonyl(decafluorotolan)bis(triphenylphosphine)di*-

cobalt(0) (0.51 g., 67%) (Found: C, 58.4; H, 3.1; Co, 10.1. $C_{54}H_{30}Co_2F_{10}O_4P_2$ requires C, 58.3; H, 2.7; Co, 10.3%), m. p. 209–211° (decomp.).

(e) Thermal decomposition. The complex (0.72 g., 1.20 g)mmoles), in anhydrous benzene (15 ml.), was heated in a sealed tube (300 ml.) at 180° for 16 hr. Carbon monoxide (5.7 mmoles) was evolved, and the walls of the tube were coated with a metallic mirror. The reaction mixture was filtered, and the filtrate was chromatographed on alumina. Benzene eluted a red solid, which was recrystallised from chloroform, to give red crystals of tetrakispentafluorophenylcyclopentadienone (perfluorotetracyclone) (0.31 g., 50%) (Found: C, 46.9; F, 51.2. C₂₉F₂₀O requires C, 46.8; F, 51·1%), m. p. 231-231·5°. An unidentified brown solid (0.07 g.) was eluted with methanol. The mass spectrum of the cyclopentadienone shows the following main peaks [m/e (rel. int.) (probable identity, P = parent)]: $744 \pm \bar{3}$ (91) (P)⁺; 716 (64) (P - CO)⁺; 644 (23) (P - C_2F_4)⁺; 549 (27) [(C_6F_5)₃ C_4]⁺; 537 (16) [(C_6F_5)₃ C_3]⁺; 358 (100) $[(P - CO)^{2+} \text{ or } (C_{14}F_{10})^+].$

Reaction of Decafluorotolan with Iron Carbonyls.--(a) Iron pentacarbonyl. Decafluorotolan (1.76 g., 4.9 mmoles) and iron pentacarbonyl (1.40 g., 7.1 mmoles), in light petroleum (b, p. $40-60^{\circ}$) (100 ml.), were irradiated for 18 hr. (Hanovia 500 w; positioned so that gentle refluxing was maintained). The products were chromatographed on neutral alumina (Woelm), with light petroleum (b. p. 60-80°), ether, and methanol as eluents. The light petroleum fraction was sublimed in vacuo, to give decafluorotolan (0.51 g., 29%), m. p. 121-121.5°, and a solid residue, which was recrystallised from light petroleum (b. p. 100-120°), to yield yellow crystals of the iron complex (XIV) (0.53 g., 21%) [Found: C, 41.0; Fe, 10.6%; M (vapour pressure osmometer, in C_6H_6), 1022. $C_{34}F_{20}Fe_2O_6$ requires C, 40.9; Fe, 11.1%; M, 996], decomp. 200°. The ether fraction contained red crystals of the cyclopentadienone (XIII) (0.042 g., 2%), m. p. 232-233°, identified by i.r. spectroscopy.

(b) Iron dodecacarbonyl. (i) In refluxing benzene. Decafluorotolan (2.50 g., 7.0 mmoles) and iron dodecacarbonyl (2.52 g., 5.0 mmoles) were heated under reflux in anhydrous benzene (60 ml.) for 6 hr. The colour changed from dark green to dark red-brown. The reaction mixture was worked up as described above, to give decafluorotolan (0.20 g., 8%), the complex (XIV) (1.10 g., 32%), the cyclopentadienone (XIII) (0.25 g., 10%), m. p. 232—233°, and an unidentified methanol fraction (0.2 g.). (ii) At 140°. Decafluorotolan (2.50 g., 7.0 mmoles), iron dodecacarbonyl (1.50 g., 3.00 mmoles), and anhydrous benzene (25 ml.) were heated in a sealed tube at 140—150° for 20 hr. Chromatography on alumina gave the complex (XIV) (1.57 g., 45%) and a methanol fraction (0.99 g.).

Reactions of the Iron Complex (XIV).—(a) With bromine. A solution of the complex (1.07 g., 1.08 mmoles) in carbon tetrachloride (20 ml.) was heated under reflux for 3 hr. with bromine (3.1 g., 17.2 mmoles), then treated with saturated aqueous sodium pyrosulphite; the organic phase was washed with water (4×50 ml.), dried (MgSO₄), and evaporated to dryness. The residue was extracted with hot light petroleum (b. p. 40—60°), and the residue from this extraction was recrystallised from chloroform, to give red crystals

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of the cyclopentadienone (XIII) (0.35 g., 42%), m. p. 232— 233°, identified by i.r. spectroscopy. Chromatography of the light petroleum extract yielded a waxy solid (*ca.* 20% yield) which could not be adequately purified.

(b) With sulphur. A solution of the complex (0.97 g., 0.97 minole) and sulphur (0.08 g., 2.47 mg.-atoms) in anhydrous benzene (40 ml.) was irradiated for 20 hr. (Hanovia 500 w lamp positioned so that the solution boiled under gentle reflux). From time to time the walls of the irradiation vessel had to be cleaned to remove a black deposit

(this deposit gave H_2S on treatment with acid). The reaction mixture was filtered and evaporated, and the residue was recrystallised from light petroleum (b. p. $100-120^{\circ}$) and sublimed *in vacuo* at 140°, to give crystals of tetrakispenta-fluorophenylthiophen (0.15 g., 21%), m. p. $181-182^{\circ}$, identified by i.r. spectroscopy.

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