PERFLUOROPHENYL DERIVATIVES OF THE ELEMENTS XII*. 2,2'-DISUBSTITUTED OCTAFLUOROBIPHENYLS

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We have recently[2] described a new synthetic route to disubstituted octafluorobiphenyls, utilising the thermal disproportionation of substituted polyfluorophenyl derivatives of titanium and now wish to report some of our findings on the chemistry of several 2,2'-disubstituted octafluorobiphenyl derivatives, as shown in Fig. 1.
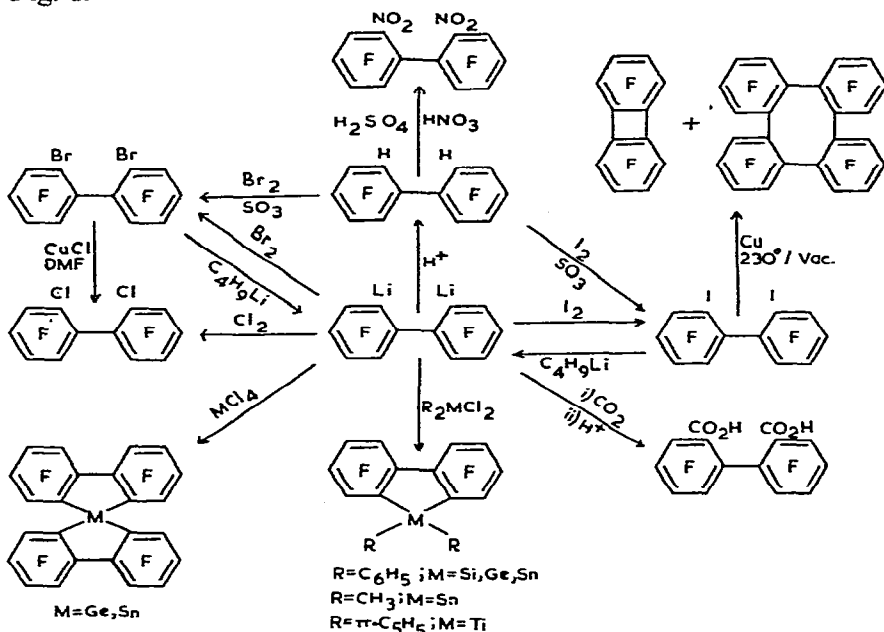

Fig. 1. Reactions of 2,2'-dilithiooctafluorobiphenyl.

2,2'-Dibromooctafluorobiphenyl has been obtained in yields up to 92% using the above coupling reaction and has proved invaluable as an intermediate in the synthesis of several other 2,2'-disubstituted octafluorobiphenyls. 2,2'-Dibromooctafluorobiphenyl can be mono- or dilithiated by lithium–bromine exchange using n-butyllithium in ether/hexane or tetrahydrofuran/hexane; hydrolysis of these lithio derivatives gives 2-hydro-2'-bromooctafluorobiphenyl and 2,2'-dihydrooctafluoro-

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* For Part XI see Ref. 1.

biphenyl respectively. There is a great tendency toward dilithiation as shown by the reaction of 2,2'-dibromooctafluorobiphenyl with one equivalent of n-butyllithium which results, after hydrolysis, in a mixture of 2,2'-dihydrooctafluorobiphenyl, 2-hydro-2'-bromooctafluorobiphenyl and unreacted 2,2'-dibromooctafluorobiphenyl. In the single ring systems, 1,2-dibromotetrafluorobenzene resists dilithiation under our conditions whereas 1,4-dibromotetrafluorobenzene reacts with one equivalent of n-butyllithium to give a mixture of 1,4-dilithiotetrafluorobenzene and 1-lithio-4-bromotetrafluorobenzene but gives only the dilithiated product with two equivalents of n-butyllithium[3]; thus 2,2'-dibromooctafluorobiphenyl resembles 1,4-dibromo-tetrafluorobenzene in its reaction with n-butyllithium.

2,2'-Dilithiooctafluorobiphenyl reacts with chlorine, bromine or iodine to give the corresponding 2,2'-dihalooctafluorobiphenyl in high yield together with a small quantity of the corresponding 2-hydro-2'-halooctafluorobiphenyl arising from adventitious hydrolysis of the intermediate 2-lithio-2'-halooctafluorobiphenyl.

The hydrogen atoms of 2,2'-dihydrooctafluorobiphenyl readily undergo electrophilic substitution by Br^+, I^+ and NO_2^+. Thus with bromine or iodine in 20% oleum the corresponding 2,2'-dihalooctafluorobiphenyl is obtained in 60–90% yields; and with a 2 : 1 mixture of concentrated sulphuric and nitric acids, either one or both hydrogen atoms are replaced, the resulting mixture of 2,2'-dinitrooctafluorobiphenyl and 2-hydro-2'-nitrooctafluorobiphenyl being easily separated by fractional vacuum sublimation.
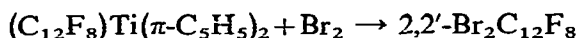
By reacting 2,2'-dilithiooctafluorobiphenyl with chlorides of Group IV elements, we have obtained the series of organometallic heterocyclic compounds shown in Table 1. These compounds are monomeric in benzene or chloroform at 37°, are air and water stable, and have high thermal stability, *e.g.* bis(octafluorobiphenyl-ene)germane was recovered almost quantitatively after heating in an evacuated sealed tube for $2\frac{1}{2}$ days at 400° followed by four hours at 500° when very slight charring was observed; the metal–carbon σ bonds are only slowly cleaved by halogens, thus after heating with iodine in an evacuated sealed tube for 3 days at 230° followed by one day

TABLE 1

ORGANOMETALLIC HETEROCYCLIC COMPOUNDS DERIVED FROM 2,2'-DILITHIOOCTAFLUOROBIPHENYL

Compound	Yield (%)	M.p. (°C)	Analysis found/calcd.			
			C(%)	H(%)	F(%)	Mol.wt.
$(C_{12}F_8)_2Ge$	48	230–232°	43.5	0.0	45.9	647
			43.4	0.0	45.7	665
$(C_{12}F_8)_2Sn$	17	227–229°	40.6	0.1	43.2	697
			40.6	0.0	42.8	711
$(C_5H_5)_2Ti(C_{12}F_8)$	25	>230°	56.0	1.9	32.0	
			55.7	2.1	32.05	
$(C_{12}F_8)Ge(C_6H_5)_2$	50	139–141°	55.0	2.1	28.9	517
			55.1	1.9	29.1	523
$(C_6H_5)_2Sn(C_{12}F_8)$	24	131–133°	50.7	1.7	26.8	562
			50.7	1.8	26.7	569
$(C_6H_5)_2Si(C_{12}F_8)$	20	147–149°	60.1	2.2	32.0	475
			60.3	2.1	31.8	478
$(CH_3)_2Sn(C_{12}F_8)$	low		38.1	1.9	33.0	
			37.8	1.4	34.2	

at 340°, bis(octafluorobiphenylene)germane had but partially reacted to give 2,2'-diiodooctafluorobiphenyl and 2-hydro-2'-iodooctafluorobiphenyl.

With di-π-cyclopentadienyltitanium dichloride, 2,2'-dilithiooctafluorobiphenyl reacts to give the novel heterocyclic titanium derivative $(C_{12}F_8)Ti(\pi\text{-}C_5H_5)_2$. This compound has reasonably high thermal stability, being decomposed *in vacuo* only after 24 hours at temperatures in excess of 330° ; cleavage of the metal–carbon σ bond takes place with bromine in refluxing carbon tetrachloride and with refluxing aqueous hydrogen chloride:

$$(C_{12}F_8)Ti(\pi\text{-}C_5H_5)_2 + Br_2 \rightarrow 2,2'\text{-}Br_2C_{12}F_8$$

$$(C_{12}F_8)Ti(\pi\text{-}C_5H_5)_2 + HCl \text{ aq.} \rightarrow 2,2'\text{-}H_2C_{12}F_8$$

Although 2,2'-dibromooctafluorobiphenyl does not react when heated at 230° *in vacuo* with copper bronze, the corresponding reaction with 2,2'-diiodooctafluorobiphenyl gives a mixture of compounds from which octafluorobiphenylene and perfluorotetraphenylene were isolated by fractional vacuum sublimation[4]. A similar experiment in which 1,2-diiodotetrafluorobenzene was used in lieu of 2,2'-diiodooctafluorobiphenyl gave a mixture containing the rather interesting perfluorotriphenylene[5]

TABLE 2

MASS SPECTRA OF PERFLUOROPHENYLENES

Mass number	Assignment	$C_{12}F_8$	$C_{18}F_{12}$	$C_{24}F_{16}$
594	$^{13}C_2^{12}C_{22}F_{16}^+$			7.0
593	$^{13}C^{12}C_{23}F_{16}^+$			28.8
592	$C_{24}F_{16}^+$			100.0
524	$^{13}C^{12}C_{22}F_{13}^+$			6.5
523	$C_{23}F_{13}^+$			24.2
492	$C_{22}F_{12}^+$			13.0
485	$C_{23}F_{11}^+$			4.2
445	$^{13}C^{12}C_{17}F_{12}^+$		21.8	
444	$C_{18}F_{12}^+$		100.0	
413	$C_{17}F_{11}^+$		12.5	
406	$C_{18}F_{10}^+$		7.5	
382	$C_{16}F_{10}^+$		5.0	
375	$C_{17}F_9^+$		12.5	
344	$C_{16}F_8^+$		7.8	
313	$C_{15}F_7^+$		4.7	
297	$^{13}C^{12}C_{11}F_8^+$	14.0		
296	$C_{12}F_8^+/C_{24}F_{16}^{++}$	100.0	15.0	3.9
277	$C_{12}F_7^+$	8.9		
265	$C_{11}F_7^+$	11.2		
261.5	$C_{23}F_{13}^{++}$			4.6
258	$C_{12}F_6^+$	5.2		
246	$C_{11}F_6^+$	22.5		17.0
227	$C_{11}F_5^+$	17.0		
222	$C_9F_6^+/C_{18}F_{12}^{++}$		12.2	
196	$C_{10}F_4^+$	7.2		
177	$C_{10}F_3^+$	5.1		
165	$C_9F_3^+$	4.7		
148	$C_6F_4^+/C_{12}F_8^{++}$	6.7		

in addition to octafluorobiphenylene and perfluorotetraphenylene. It was suggested[6,7] that, due to steric compression, perfluorotriphenylene might be incapable of existence whereas its apparent stability supports the conclusion, drawn by Gray[8] from a study of the ultra-violet spectra of substituted biphenyls, that the steric requirements of the fluorine atom may well be little different to those of hydrogen. Mass spectral data for these polyfluorophenylenes are given in Table 2.

An interesting feature of the mass spectra of these polyfluorophenylenes and other polyfluoroaromatic compounds[9] is that $(p - CF_3)^+$ is one of the most prominent ions; a metastable peak corresponding to the loss of CF_3 is also to be observed which suggests that at least part of the CF_3 is lost in a single step, presumably by the migration of two fluorine atoms.

Replacement of the bromine atoms in 2,2'-dibromooctafluorobiphenyl by the use of reagents other than n-butyllithium has proved to be difficult. When refluxed in dimethylformamide with cuprous chloride[10] for four hours, a mixture of products was obtained. Analytical vapour phase chromatography indicated the presence of six compounds including 2,2'-dichlorooctafluorobiphenyl, 2-hydro-2'-chlorooctafluoro-biphenyl and unreacted 2,2'-dibromooctafluorobiphenyl; the other three compounds were not identified but the retention time of the fifth component indicated the possib-ility of 2-bromo-2'-chlorooctafluorobiphenyl. On heating 2,2'-dibromooctafluoro-biphenyl with zinc in refluxing glacial acetic acid for 15 hours, only partial reduction occurred to give a mixture of 2,2'-dihydrooctafluorobiphenyl, 2-hydro-2'-bromoocta-fluorobiphenyl and unreacted 2,2'-dibromooctafluorobiphenyl in the approximate ratios 1/1.8/2.

Reaction of 2,2'-dilithiooctafluorobiphenyl with gaseous carbon dioxide followed by hydrolysis gives rise to the formation of octafluorodiphenic acid of which we have prepared the disodium, calcium and mercuric salts. The latter is easily decarboxylated at 280° to give a colourless crystalline solid which sublimes at 300° under atmospheric pressure: the infrared spectrum shows carbon–mercury stretching frequencies and analysis corresponds to $[(C_{12}F_8)Hg]_x$. A molecular weight determin-ation in acetone of ~ 2040 shows the compound to be tetrameric being, presumably, analogous to $[(C_{12}H_8)Hg]_4$[11].

In order to discover something about the organometallic titanium intermediate formed in the coupling reaction used in the polyfluorobiphenyl synthesis, we have investigated the effect of altering the ratio $TiCl_4/C_6F_5Li$ in the formation of deca-fluorobiphenyl. Our results indicate that this ratio must be $> \frac{1}{4}$ for any decafluoro-biphenyl to be obtained, as shown in Fig. 2. We have studied this particular reaction since the polyfluorobenzene (hydrolysis) derivative formed in lieu of decafluoro-biphenyl, i.e. pentafluorobenzene, is sufficiently volatile to be removed with the solvent and thus does not contaminate the resultant decafluorobiphenyl.

In the reaction where the ratio $TiCl_4/C_6F_5Li$ was $\frac{1}{4}$, the orange ether/hexane solution was siphoned off from the white precipitate of lithium chloride present and removal of solvent gave an orange-yellow viscous liquid. The latter was immediately hydrolysed on exposure to air to give pentafluorobenzene and hydrated titanium dioxide, and gave a virtually quantitative yield (based on bromopentafluorobenzene initially taken) of bis(pentafluorophenyl)mercury[6] when a solution in benzene was shaken for several hours with excess mercuric chloride. It thus seems probable that the above viscous liquid contained tetrakis(pentafluorophenyl)titanium, $Ti(C_6F_5)_4$,
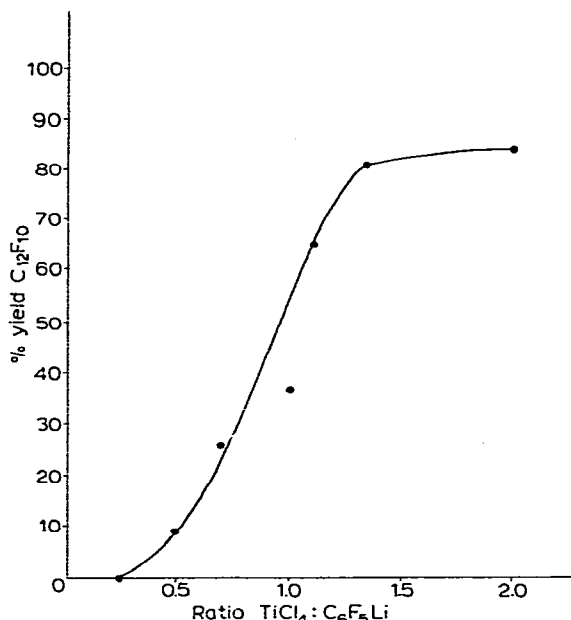
Fig. 2. Variation of the yield of decafluorobiphenyl with the ratio $TiCl_4 : C_6F_5Li$.

and the absence of decafluorobiphenyl would indicate that the organometallic intermediate formed in the coupling reaction is not $Ti(C_6F_5)_4$ but more likely $Ti(C_6F_5)_2Cl_2$. The latter could be visualised to disproportionate with rise in temperature to give decafluorobiphenyl and $TiCl_2$ which would be oxidised by further $TiCl_4$ to give $TiCl_3$; work carried out by Razuvaev on phenyl derivatives of titanium supports this[12]. The chance of formation of $Ti(C_6F_5)_2Cl_2$ as opposed to $Ti(C_6F_5)_4$ probably increases as the ratio $TiCl_4/C_6F_5Li$ becomes greater and thus the yield of decafluorobiphenyl would also increase since $Ti(C_6F_5)_4$ apparently does not disproportionate at room temperature.

When $TiCl_4/LiC_6F_5$ ratios of about $\frac{1}{10}$ are employed, side-products are obtained on hydrolysis which arise from the thermal decomposition of pentafluorophenyllithium:

$$LiC_6F_5 \xrightarrow{-LiF} [C_6F_4] \xrightarrow{LiC_6F_5} 2\text{-}LiC_6F_4C_6F_5 \qquad \text{(ref. 9, 13)}$$

Further loss of lithium fluoride by 2-lithiononafluorobiphenyl[1] followed by addition of undecomposed pentafluorophenyllithium occurs to give two isomeric terphenyl derivatives one of which can again lose lithium fluoride intramolecularly:
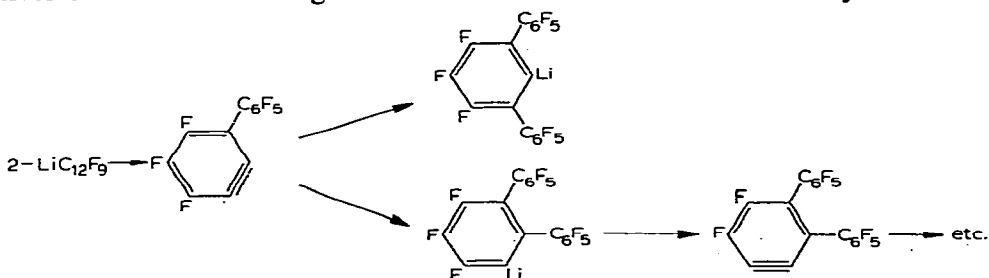
this type of benzyne formation followed by addition of pentafluorophenyllithium can apparently happen five times round the one benzene ring[15]. The lithium compounds in the case of these titanium tetrachloride reactions were detected as their hydrolysis products.

The ^{19}F nuclear magnetic resonance spectra of the 2,2'-disubstituted octafluorobiphenyls discussed above were recorded at 94.1 Mc/s on a Varian HA 100 spectrometer. Four distinct groups of lines were obtained and can be assigned to four magnetically different fluorine atoms of one half of the symmetrical octafluorobiphenyl:

$$F_3 \equiv F_3', F_4 \equiv F_4' \text{ etc.}$$
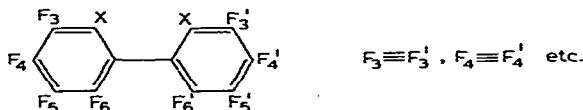
In the case of 2,2'-dihydrooctafluorobiphenyl, however, only three groups of lines are observed due to overlap of the resonances due to F_4 and F_5. Use of a combination of the expected chemical shifts calculated by use of substitution parameters[9,13,14], and the observed coupling constants enable the groups of lines to be assigned to the four fluorine atoms as shown in Table 3.

TABLE 3

CHEMICAL SHIFTS OF THE FLUORINE ATOMS IN 2,2'-DISUBSTITUTED OCTAFLUOROBIPHENYLS, 2,2'-$X_2C_{12}F_8$ ± 0.1 ppm relative to $CFCl_3$.

X	F_3	F_4	F_5	F_6
Cl	136.8	151.1	156.2	136.0
Br	127.6	150.6	154.8	134.0
I	112.9	150.5	153.2	133.3
H	139.7	154.4		138.9
NO$_2$	142.2	145.5	146.7	134.6
CO$_2$H	137.5	152.6	154.0	· 136.8

EXPERIMENTAL

Reactions involving organolithium reagents were carried out under an atmosphere of dry nitrogen. Micro-analyses were performed by Dr. A. Bernhardt, Mülheim, Ruhr and the molecular weights were recorded on a Mechrolab vapour phase osmometer by Miss Sylvia Park of this laboratory. We gratefully acknowledge gifts of polyfluorobenzenes by the Imperial Smelting Corporation Ltd., and of germanium halides from the Organisch Chemisch Instituut T.N.O. Utrecht. The preparations of 2,2'-dibromo- and 2,2'-dihydrooctafluorobiphenyl have been described previously[2].

The reaction of 2,2'-dihydrooctafluorobiphenyl with bromine in oleum
2,2'-Dihydrooctafluorobiphenyl (2.98 g, 0.01 mole), bromine ($\sim$3 ml), aluminium tribromide (0.5 g) and *ca.* 20% oleum (25 ml) were heated at 60–75° for 6 h. The resultant mixture was then cooled and added to 500 g of crushed ice; the brown

solid obtained was filtered off, dissolved in ether and washed with sodium carbonate and sodium thiosulphate solutions. After drying the ether solution ($MgSO_4$) the solvent was removed and the resultant 2,2'-dibromooctafluorobiphenyl purified by vacuum sublimation; yield 2.8 g (61%).

The reaction of 2,2'-dihydrooctafluorobiphenyl with iodine in oleum

The above process was repeated using a mixture of 2,2'-dihydrooctafluoro-biphenyl (2.98 g), iodine (6 g), and *ca.* 20% oleum (30 ml). The yellow-white crystalline solid was sublimed under vacuum at 60–75° (10^{-4} mm) to give faint yellow 2,2'-di-iodooctafluorobiphenyl, m.p. 80–82°. Yield 5 g or 91%. (Found: C, 26.5; H, 0.0; F, 27.6; I, 46.3; mol. wt., 547. $C_{12}F_8I_2$ calcd.: C, 26.2; H, 0.0; F, 27.6; I, 46.2%; mol. wt., 550.)

The reaction of 2,2'-dihydrooctafluorobiphenyl with concentrated nitric/sulphuric acids

A mixture of 2,2'-dihydrooctafluorobiphenyl (4.3 g), concentrated nitric acid (15 ml) and concentrated sulphuric acid (25 ml) was heated at about 80° for 8 h. The resulting mixture was poured onto crushed ice, extracted with ether and washed with sodium hydroxide solution. The ether solution was then dried ($MgSO_4$) when removal of solvent gave an orange-yellow oil. Vacuum sublimation, 40–55° (10^{-4} mm) gave an off-white solid, 2-hydro-2'-nitrooctafluorobiphenyl, m.p. 41–45°. Yield 1 g. (Found: C, 42.0; H, 0.2; F, 44.1; N, 4.2; mol. wt., 340. $C_{12}F_8HNO_2$ calcd.: C, 42.0; H, 0.3; F, 44.3; N, 4.1%; mol. wt., 343.)

Further vacuum sublimation 95–105° gave a yellow solid, 2,2'-dinitroocta-fluorobiphenyl, m.p. 117–120°. Yield 0.8 g. (Found: C, 36.9; H, 0.1; F, 38.9; N, 7.3. $C_{12}F_8N_2O_4$ calcd.: C, 37.1; H, 0.0; F, 39.1; N, 7.2%.)

Lithiation of 2,2'-dibromo- and 2,2'-diiodooctafluorobiphenyl using butyllithium

Treatment of 2,2'-dibromo- or 2,2'-diiodooctafluorobiphenyl (on the 4–5 g scale) in an ether/hexane solvent mixture at −78° with about 2.1 equivalents of n-butyllithium, followed by stirring for 1 h results in the virtually quantitative form-ation of 2,2'-dilithiooctafluorobiphenyl. This was demonstrated by the addition of water to the system when the hydrolysis product, 2,2'-dihydrooctafluorobiphenyl, could be isolated in yields of 96–98%. The lithiation occurs to the same extent in tetrahydrofuran/hexane solvent at −78°.

The reaction of 2,2'-dilithiooctafluorobiphenyl with halogens

(i) *Chlorine.* 2,2'-Dilithiooctafluorobiphenyl was prepared as above from 2,2'-dibromooctafluorobiphenyl (2.28 g). Gaseous chlorine was passed through the ether/hexane solution for 15 min, after which the mixture was allowed to stand at room temperature for 2 h. Water was added, the organic solution separated, washed with sodium thiosulphate solution, dried ($MgSO_4$), filtered and then the solvent removed; a light-brown solid (1.84 g) was obtained. Vapour phase chromatography indicated two components, the first eluted in about 5% of the total product; these were separated using preparative vapour phase chromatography. The first to elute was liquid at room temperature and was judged to be 2-hydro-2'-chlorooctafluorobiphenyl from its infrared spectrum. The second component was the white solid 2,2'-dichloroocta-fluorobiphenyl, m.p. 103.5–104.5°. Yield of $C_{12}F_8Cl_2$ 95%. (Found: C, 39.0; H, 0.0;

F, 41.7; Cl, 19.5. $C_{12}F_8Cl_2$ calcd.: C, 39.3; H, 0.0; F, 41.4; Cl, 19.3%.)

(ii) *Bromine.* The above procedure was repeated using bromine ($\sim$1.5 ml), and preparing the 2,2'-dilithiooctafluorobiphenyl from 4.56 g of 2,2'-dibromooctafluorobiphenyl. The reaction proceeded in almost quantitative yield giving 4.5 g of product which was 2,2'-dibromooctafluorobiphenyl plus trace quantities of 2,2'-dihydrooctafluorobiphenyl and 2-hydro-2'-bromooctafluorobiphenyl, the latter being detected by vapour phase chromatography.

(iii) *Iodine.* 2,2'-Diiodooctafluorobiphenyl was obtained in 92% yield together with trace quantities of 2,2'-dihydrooctafluorobiphenyl and 2-hydro-2'-iodooctafluorobiphenyl.

Preparation of diphenyl(octafluorobiphenylene)germane

n-Butyllithium (12.5 ml of 1.56 molar solution in hexane) was added to 2,2'-dibromooctafluorobiphenyl (4.56 g; 0.02 mole) in 50 ml of ether at $-78°$ and the mixture stirred for 2 h. Diphenyldichlorogermane (2.98 g; 0.01 m) in 20 ml ether was added after which the reaction flask was allowed to attain room temperature and stirring continued for 3 h. A white precipitate and a yellow solution resulted; the solution was syphoned out of the vessel and the solvent removed under vacuum to yield a yellow-brown solid. Recrystallisation from ethanol followed by vacuum sublimation at 120–130° (10^{-4} mm) gave pure diphenyl (octafluorobiphenylene)-germane, 2.6 g, as a white solid.

The other compounds listed in Table 1 and dicyclopentadienyl(octafluorobiphenylene)titanium were prepared in similar fashion.

The reaction of 2,2'-diiodooctafluorobiphenyl with copper

2,2'-Diiodooctafluorobiphenyl (*ca.* 3 g) and activated copper bronze (*ca.* 3 g) were heated in an evacuated sealed tube at 230° for 24 h. Extraction of the soluble contents of the tube with ether, followed by filtration and removal of solvent gave a light-brown solid; VPC analysis of this solid showed the presence of four components eluted after 2.3, 2.8, 6.6 and 18.0 min (silicone column, 206°; helium flow rate, 105 cc·min^{-1}). The first peak was found to be due to 2,2'-dihydrooctafluorobiphenyl and the peak at 6.6 min. was probably 2-iodo-2'-hydrooctafluorobiphenyl as deduced from its infrared spectrum. When the copper bronze was thoroughly dried by heating under vacuum before reaction it was found that the VPC trace showed only the peaks at 2.8 and 18.0 min. Vacuum sublimation of the ether-extracted products at room temperature (10^{-4} mm) gave perfluorobiphenylene as a white solid (responsible for the VPC peak at 2.8 min); further sublimation at 130–160° (10^{-4} mm) gave perfluorotetraphenylene as a white solid which accounted for the VPC peak at 18 min. Both compounds analysed correctly for perfluorophenylenes, $(C_6F_4)_x$ where $x = 2$ and 4 respectively; see Table 4. The reaction between 1,2-diiodotetrafluorobenzene and copper was carried out as above; fractional vacuum sublimation gave mainly the white solid, perfluorotriphenylene, volatile at 50° in a vacuum (10^{-4} mm). Mass spectral analyses showed the presence of polyphenylenes with $x = 2$ through 6 in the products.

Reaction of 2,2'-dilithiooctafluorobiphenyl and carbon dioxide

n-Butyllithium (10 ml of 2.7 molar hexane solution) was added to 2,2'-di-

TABLE 4

EXPERIMENTAL DATA FOR THE PERFLUOROPOLYPHENYLENES, $(C_6F_4)_x$ $(x = 2, 3, 4)$

Phenylene[a]	M.p. (°C)	Analysis found/calcd.			Parent ion in mass spectrum
		C(%)	H(%)	F(%)	
Octafluoro-biphenylene	100–101.5	48.7	0.0	51.3	$C_{12}F_8^+$
		48.7	0.0	51.3	
Perfluoro-triphenylene	102–104	48.8	0.15	51.1	$C_{18}F_{12}^+$
		48.7	0.0	51.3	
Perfluoro-tetraphenylene	249–251	48.7	0.0	51.5	$C_{24}F_{16}^+$
		48.7	0.0	51.3	

[a] Yields ca. 10%.

bromooctafluorobiphenyl (5.71 g) in ether (100 ml) at $-78°$ and stirred for 1 h. The cold bath was removed and carbon dioxide passed into the solution for 2 h at room temperature. Dilute hydrochloric acid (100 ml of 6 N) was added, stirred, the yellow ether layer separated, extracting the aqueous layer with further ether portions. The combined ether portions were dried ($MgSO_4$) and solvent evaporated to give a yellow-brown solid. Addition of pentane gave an off-white flaky solid. Recrystallisation from hot benzene gave a colourless feathery crystalline solid; vacuum sublimation, 120–130°, gave the white microcrystalline solid octafluorodiphenic acid, m.p. 239.5–241°. Yield 3.2 g (66%). (Found: C, 43.6; H, 0.5; F, 39.2; mol. wt., 384; acid equivalent, 192.6. $C_{14}H_2F_8O_4$ calcd.: C, 43.5; H, 0.5; F, 39.4%; mol. wt., 386; acid equivalent, 193.1.)

Preparation of the tetrameric mercurial $[(C_{12}F_8)Hg]_4$

A solution of mercuric acetate (0.64 g, ~0.002 mole) in water/acetic acid (25/0.5 ml) was slowly added to a solution of octafluorodiphenic acid (0.772 g, 0.002 mole) in water (60 ml)/ethanol (15 ml). The immediately-formed fine white precipitate was filtered off and dried at 100° for several hours; yield 0.8 g. The carboxylate bands of the compound's infrared spectrum were similar to those of mercuric pentafluorobenzoate[16]. The mercuric salt derived from octafluorodiphenic acid was heated for 24 h at 300° in an open tube when colourless needle-like crystals of the mercurial were obtained on the side walls of the tube; m.p. >370°. (Found: C, 28.6, 30.0; H, 0.0, 0.0; F, 28.5, 31.4; mol. wt., 2038. $[(C_{12}F_8)Hg]_4$ calcd.: C, 29.0; H, 0.0; F, 30.6%; mol. wt., 1988.)

Reaction of 2,2'-dibromooctafluorobiphenyl with cuprous chloride

2,2'-Dibromooctafluorobiphenyl (1 g), cuprous chloride (0.95 g) and dimethylformamide (25 ml) were heated under reflux for 4 h. The mixture was added to water, filtered and extracted with ether, washing the precipitate obtained with further portions of ether. The combined ether extracts were dried ($MgSO_4$), filtered and solvent removed to give a brown solid. Analytical vapour phase chromatography indicated six components with the second, fifth and sixth components constituting most of the mixture and in the approximate ratios 1/1.2/1.2. Addition of authentic samples indicated that the first, second and sixth components were respectively

2-hydro-2'-chlorooctafluorobiphenyl, 2,2'-dichlorooctafluorobiphenyl and unreacted 2,2'-dibromooctafluorobiphenyl. A repeat experiment in which the starting mixture was refluxed overnight yielded only four components; the fourth and sixth components obtained above were now absent and the main component was 2,2'-dichloroocta-fluorobiphenyl.

Infrared spectra

There were recorded on a Grubb–Parsons double beam grating Spectrophoto-meter by Mr P. Cook. Peaks are reported in cm^{-1} for mulls in nujol and hexachloro-butadiene except where stated otherwise.

$2,2'-I_2C_{12}F_8$. 1626 w, 1495 s, 1475 s, 1456 s, 1107 s, 1078 msh, 1071 m, 1029 s, 1019 s, 941 m, 805 s, 799 s, 767 w, 712 m, 706 m.

$2,2'-Cl_2C_{12}F_8$. 1626 w, 1618 w, 1502 s, 1484 ssh, 1476 s, 1466 s, 1428 w, 1117 m, 1090 w, 1080 w, 1041 s, 1038 ssh, 1031 s, 1010 wsh, 950 m, 877 s, 871 s, 782 w, 773 w, 718 s, 701 msh.

$2,2'-(NO_2)_2C_{12}F_8$. 1613 m, 1555 ssh, 1546 s, 1538 ssh, 1517 ssh, 1511 s, 1502 ssh, 1475 sbr, 1357 s, 1348 ssh, 1337 ssh, 1279 m, 1136 m, 1126 m, 1103 s, 1053 sbr, 973 m, 936 m, 773 s, 767 s, 750 w, 723 s, 703 w.

$2-H-2'-NO_2C_{12}F_8$. 1631 m, 1621 m, 1558 ssh, 1548 s, 1527 ssh, 1511 s, 1484 s, 1466 ssh, 1458 msh, 1366 s, 1333 m, 1277 m, 1203 m, 1140 w, 1112 s, 1081 s, 1075 msh, 1056 w, 1025 s, 950 m, 927 m, 864 m, 858 w, 769 s, 739 s, 723 w, 700 w, 688 m.

$2,2'-(COOH)_2C_{12}F_8$. 2985 mvbr, 1754 s, 1664 w, 1637 m, 1616 m, 1524 w, 1513 s, 1495 ssh, 1484 s, 1443 m, 1412 s, 1344 m, 1316 w, 1287 m, 1245 s, 1229 s, 1127 m, 1124 wsh, 1099 s, 1048 s, 969 m, 933 w, 903 w, 848 mbr, 825 wbr, 750 w, 733 w, 716 m, 699 msh, 694 s.

$C_{12}F_8$. 1661 w, 1656 wsh, 1634 w, 1490 s, 1466 s, 1456 ssh, 1439 msh, 1385 w, 1379 w, 1333 w, 1321 msh, 1305 s, 1101 s, 1083 s, 1076 s, 861 m, 685 m, 667 m, 628 w.

$C_{24}F_{16}$. 1634 w, 1508 s, 1475 s, 1462 ssh, 1401 w, 1385 w, 1318 w, 1274 w, 1104 s, 1096 wsh, 1073 m, 1063 ssh, 1056 s, 970 w, 963 m, 752 w, 719 s, 699 m.

$(C_{12}F_8)Si(C_6H_5)_2$. 1618 w, 1595 w, 1486 s, 1462 s, 1456 ssh, 1429 s, 1383 msh, 1361 w, 1311 m, 1297 m, 1247 m, 1238 msh, 1160 w, 1119 m, 1103 s, 1072 s, 1037m, 1028 wsh, 998 w, 972 w, 921 m, 855 w, 848 w, 781 w, 742 m, 728 m, 714 m, 707 s, 694 s, 685 wsh, 644 w.

$(C_{12}F_8)Ge(C_6H_5)_2$. 1626 w, 1603 m, 1580 wsh, 1484 s, 1464 s, 1429 s, 1399 ssh, 1379 s, 1350 m, 1333 m, 1302 s, 1285 m, 1258 w, 1252 m, 1238 w, 1188 w, 1160 w, 1094 s, 1059 sbr, 1031 s, 1028 ssh, 998 m, 921 m, 823 m, 786 w, 733 s, 724 m, 706 s, 693 s, 678 w, 640 w, 595 w.

$(C_{12}F_8)Sn(C_6H_5)_2$. 1626 w, 1605 w, 1587 w, 1477 s, 1453 ssh, 1449 s, 1429 s, 1381 w, 1333 m, 1297 m, 1282 m, 1255 w, 1244 m, 1225 w, 1193 w, 1160 w, 1096 s, 1078 m, 1073 m, 1053 s, 1029 m, 1024 msh, 998 m, 913 m, 855 w, 801 w, 770 w, 731 s, 720 m, 699 s, 694 msh, 637 w, 588 w.

$(C_{12}F_8)_2Ge$. 1618 w, 1603 w, 1490 s, 1471 s, 1460 ssh, 1408 w, 1385 w, 1372 w, 1350 w, 1312 m, 1299 m, 1253 m, 1238 w, 1153 w, 1096 s, 1075 ssh, 1067 s, 1044 m, 925 m, 837 m, 780 w, 727 w, 711 s, 645 w.

$(C_{12}F_8)_2Sn$. 1618 w, 1595 m, 1488 s, 1462 s, 1451 ssh, 1408 w, 1366 w, 1337 w, 1302 m, 1295 wsh, 1252 msh, 1247 m, 1107 s, 1063 ssh, 1057 s, 1037 s, 919 wsh, 913 m, 815 w, 773 w, 705 m, 641 w, 588 w.

$(C_{12}F_8)Ti(\pi\text{-}C_5H_5)_2$. 1616 w, 1595 w, 1473 s, 1439 ssh, 1435 s, 1425 s, 1385 m, 1340 m, 1277 m, 1239 w, 1121 w, 1074 m, 1064 m, 1032 s, 1021 m, 1014 m, 1000 m, 909 m, 843 msh, 832 sbr, 769 w, 693 m.

$[(C_{12}F_8)Hg]_4(KBr\ disc)$. 1623 m, 1605 m, 1590 m, 1493 s, 1462 s, 1445 s, 1403 msh, 1374 w, 1364 w, 1302 s, 1282 m, 1269 m, 1127 w, 1104 ssh, 1101 s, 1063 s, 1029 msh, 1017 s, 934 m, 815 m, 799 m, 775 w, 708 m, 640 w.

SUMMARY

The preparations and reactions of several 2,2'-disubstituted octafluorobiphenyls and heterocyclic organometallic derivatives of Group IV elements and titanium are described. Some evidence is given for the organometallic titanium intermediate postulated in the coupling reaction for the syntheses of polyfluorobiphenyls.

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