PERFLUOROPHENYL DERIVATIVES OF THE ELEMENTS

II*. (PENTAFLUOROPHENYL)LITHIUM, A SOURCE OF 2-SUBSTITUTED NONAFLUOROBIPHENYLS

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Decafluorobiphenyl and various 4,4'-disubstituted octafluorobiphenyls have been synthesised previously[2]; we now report the preparation of several 2-substituted nonafluorobiphenyls.

In the preparation of bis(pentafluorophenyl)dimethyltin from (pentafluorophenyl)lithium, 2.2 mg of a white sublimable compound were isolated[3] which later proved identical to a by-product found in the preparation of Group III pentafluorophenyl derivatives[4]. This compound has been shown to be 2-bromononafluorobiphenyl and the reaction producing it to be that of (pentafluorophenyl)lithium with a fortuitous excess of bromopentafluorobenzene.

2-Bromononafluorobiphenyl is the first polyfluorobiphenyl known which contains a reactive halogen atom capable of lithium exchange with butyllithium at —78° and able to form a Grignard reagent in tetrahydrofuran; these two organometallic compounds have been shown to be useful in the preparation of other inorganic or purely organic polyfluorobiphenyl derivatives.

EXPERIMENTAL

The reactions described were carried out under an atmosphere of dry oxygen-free nitrogen; solvents were redistilled under nitrogen prior to use. All glass-ware was dried at 120° overnight. A Perkin-Elmer Fractometer (model 451), using a silicone grease column was used in the vapour phase chromatographic studies, helium being the carrier gas for analytical measurement whilst nitrogen was used for the preparative scale column. Molecular weights were recorded in benzene at 30° using a Mechrolab vapour phase osmometer (model 301A) calibrated with benzil. Dr. A. BERNHARDT Max-Planck-Institut, Mülheim, Germany performed the analyses.

The substituted polyfluorobiphenyls were initially obtained either mixed with a large quantity of brown amorphous solid or as viscous liquids, the biphenyl derivatives being soluble in excess of the halopolyfluorobenzene starting material.

Vacuum sublimation (at 10^{-4} mm) or fractional vacuum sublimation were used to obtain pure samples of the biphenyls from the amorphous solids. In the case of the viscous liquid products it was found that, although chromatography of an ether solution on a Fluorisil (60/100 mesh) column often gave good separation, gas phase

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* For Part I, see ref. 1; for Part III, see page 461.

chromatography was by far the best method of obtaining analytically pure samples. Gas phase chromatography was also very useful in analysing reaction mixtures once the retention times of the various components had been measured. Figure 1 shows the retention times, using a helium gas flow, of several perfluorophenyl and -biphenyl derivatives.

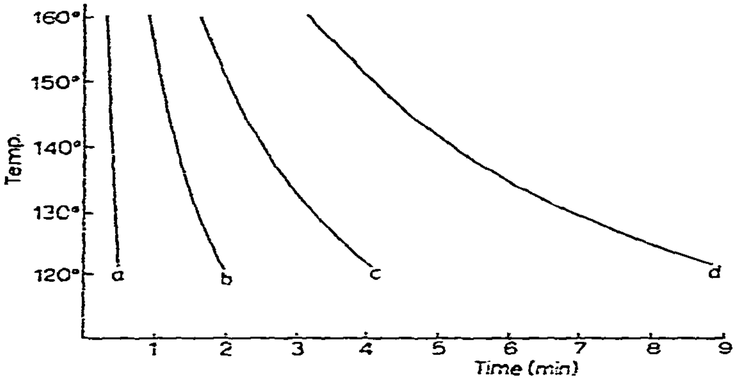


Fig. 1a. Retention times of polyfluorobenzenes: (a) hexafluorobenzene; (b) bromopentafluorobenzene; (c) iodopentafluorobenzene; (d) 1,2-dibromotetrafluorobenzene; 2 metre (¼″ diameter) silicone grease-packed column; helium flow rate, 110 cc/min.

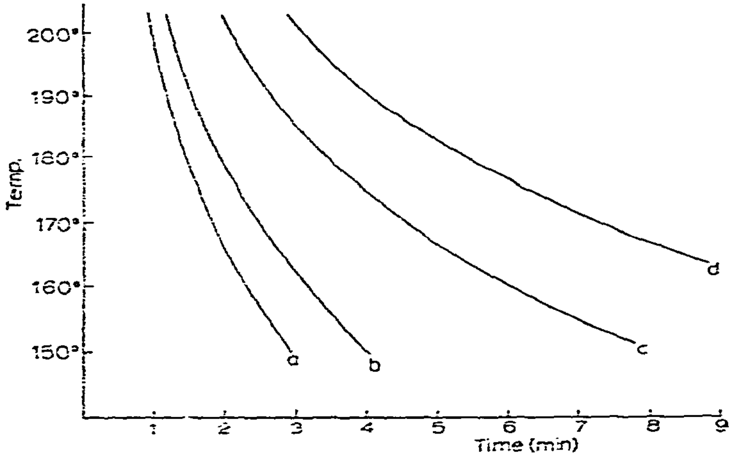


Fig. 1b. Retention times of 2-substituted nonafluorobiphenyls: (a) $C_6F_5C_6F_4F$; (b) $C_6F_5C_6F_4H$; (c) $C_6F_5C_6F_4Br$; (d) $C_6F_5C_6F_4I$; 2 metre (¼″ diameter) silicone grease-packed column; helium flow rate, 140 cc/min.

2-Bromononafluorobiphenyl, $C_6F_5C_6F_4Br$

Bromopentafluorobenzene (18 g) in 100 ml of ether was placed in a 250 ml three-necked flask fitted with a stirrer, nitrogen inlet and a serum cap. Butyllithium (20 ml of a solution containing 64 g of butyllithium in 500 ml of hexane: Foote Mineral Co) was added during 10 minutes, using a hypodermic syringe through the serum cap. The addition took place at room temperature and the reaction mixture was stirred overnight. [In other preparations the (pentafluorophenyl)lithium was added at −78° and the mixture then allowed to warm up slowly to room temperature followed by several hours stirring: there appeared to be little or no change in the yield obtained]. The brown solution was evaporated in a vacuum to give a brown solid which afforded the white 2-bromononafluorobiphenyl on sublimation at 50° in high vacuum. A further sublimation gave an analytical sample, m.p. 69–71°, yield 27% based on bromopentafluorobenzene initially taken. The reaction gives similar yields when carried out on a larger scale (10 fold increase). (Found: C, 36.5; H, 0.0; Br, 20.1; F, 43.3; mol. wt., 407. $C_{12}BrF_9$ calcd.: C, 36.5; H, 0.0; Br, 20.2; F, 43.3%; mol. wt., 395.)

2-Bromononafluorobiphenyl is soluble in the common organic solvents and in C_6F_6 and C_6F_5Br; this was found to be the case with all the polyfluorobiphenyls studied.

(Nonafluoro-2-biphenylyl)lithium and 2-hydrononafluorobiphenyl

2-Bromononafluorobiphenyl (10 g) in 100 ml of ether was placed in a 250 ml three-necked flask fitted as above. The flask was immersed in a Dewar containing alcohol at −78° and butyllithium (18 ml) was added during five minutes using a hypodermic syringe. After 15 minutes, water (50 ml) was added and the mixture warmed to room temperature. The yellow ethereal layer was separated and dried for 12 hours over $MgSO_4$. Evaporation of this solution in a vacuum yielded a light brown powder which on vacuum sublimation (10^{-4} mm) gave 2-hydrononafluorobiphenyl as a white solid. Fractional vacuum sublimation removed traces of 2-bromononafluorobiphenyl impurity; melting point of the analytical sample was 42–43°. (Found: C, 45.5; H, 0.32; F, 54.0; mol. wt., 308. $C_{12}HF_9$ calcd.: C, 45.6; H, 0.32; F, 54.1%; mol. wt., 316.)

(Nonafluoro-2-biphenylyl)magnesium bromide

(Nonafluoro-2-biphenylyl)magnesium bromide could not be prepared in ether under the same conditions used by Tatlow *et al.*[2b] to prepare (pentafluorophenyl)magnesium bromide. Refluxing the mixture under nitrogen for 12 hours also failed to give any product. The Grignard reagent can, however, be made in tetrahydrofuran.

2-Bromononafluorobiphenyl (3.9 g) in dried tetrahydrofuran (20 ml) was added to dry magnesium turnings (0.3 g) in tetrahydrofuran (10 ml). A crystal of iodine was added and the reaction started on warming; the rate of reaction was slow and all the magnesium had reacted after 5 hours. Then, distilled water (10 ml) was added and the organic products extracted with ether and dried over molecular sieve; vacuum evaporation removed the solvent and vacuum sublimation at 50° yielded 2-hydrononafluorobiphenyl (0.6 g) characterised by m.p., its infrared spectrum and its vapour phase chromatographic retention time.

2-Iodononafluorobiphenyl, $C_6F_5C_6F_4I$

The reaction between iodopentafluorobenzene (10.7 g) and butyllithium (15 ml) in 100 ml of ether, gave, with a procedure similar to that for the 2-bromo compound, a brown solution which, on evaporation in a vacuum, left a brown liquid. This liquid was chromatographed on a Fluorosil column using ether solvent to give 2-iodononafluorobiphenyl (30% yield, based on C_6F_5I). Sublimation in high vacuum afforded an analytically pure sample, m.p. 34–35°. (Found: C, 32.7; H, 0.1; F, 38.5; I, 28.65; mol. wt., 417. $C_{12}F_9I$ calcd.: C, 32.6; H, 0.0; F, 38.7; I, 28.7%; mol. wt., 442.)

Bis(nonafluoro-2-biphenylyl)mercury, $(C_6F_5C_6F_4)_2Hg$

2-Bromononafluorobiphenyl (5 g) was dissolved in dry ether, using a three-necked flask fitted with a nitrogen exit of nylon tubing[1], and butyllithium (7 ml) added at —78° over 5 minutes. Dry mercuric chloride (3.5 g) was then added as an ether slurry and the stirred mixture allowed to warm to room temperature over 3 hours; a white precipitate settled out of the solution. The nylon tubing was used to remove the supernatant liquid which on evaporation in a vacuum yielded a pale brown solid. Sublimation at 140° in high vacuum gave bis(nonafluoro-2-biphenylyl)mercury as a white solid; a further sublimation gave an analytical sample. Yield 25 %; on heating in a capillary the sample contracted at 140°, began to melt at 175° and had completely melted at 195°. (Found: C, 34.8; H, 0.1; F, 41.05; mol. wt., 811. $C_{24}F_{18}Hg$ calcd.: C, 34.7; H, 0.0; F, 41.2 %; mol. wt., 831.)

The reaction of bis(nonafluoro-2-biphenylyl)mercury with iodine

Iodine (0.5 g) and bis(nonafluoro-2-biphenylyl)mercury (0.5 g) were sealed in a glass tube and heated at 150° for 6 hours. After opening the tube, the mixture was dissolved in dry ether and the red crystals of mercuric iodide filtered off; these had a reversible transformation to yellow crystals at 140° in a capillary tube[5]. The ether solution contained iodine and 2-iodononafluorobiphenyl, the latter being identified by its infrared spectrum and its retention time in a vapour phase chromatograph.

The reaction of 1,2-dibromotetrafluorobenzene with (pentafluorophenyl)lithium

Iodopentafluorobenzene (2 g) in 10 ml of ether was placed in a three-necked flask and butyllithium (4 ml) was added at room temperature. After 5 minutes 1,2-dibromotetrafluorobenzene (2 g) was introduced and the reaction mixture stirred overnight. The ether was evaporated off in vacuum to leave a liquid. Vapour phase chromatography showed that the liquid contained 1,2-dibromotetrafluorobenzene together with roughly equal amounts of 2-bromononafluorobiphenyl and a compound thought to be $C_{12}F_8Br_2$ (work is continuing on this product and the traces of higher molecular weight material also obtained). The addition of an authentic sample of 2-bromononafluorobiphenyl to the mixture increased the chromatographic peak thought to be due to 2-bromononafluorobiphenyl; the infrared spectrum of the mixture also showed 2-bromononafluorobiphenyl to be present. Vapour phase chromatography of 1,2-dibromotetrafluorobenzene and iodopentafluorobenzene showed that the amount of bromopentafluorobenzene in either was negligible.

1-Hydro-2-bromotetrafluorobenzene, HC_6F_4Br

a). From (2-bromotetrafluorophenyl)magnesium bromide. 1,2-Dibromotetrafluorobenzene (3 g) was added to dry magnesium turnings (0.24 g) in ether, under a nitrogen atmosphere, and a crystal of iodine added. On warming, the reaction did not start and so an equal volume of dry tetrahydrofuran was added[6]. After 30 minutes of refluxing a reaction commenced and after several hours a dark brown solution remained, all the magnesium having reacted. Distilled water (10 ml) and dilute sulphuric acid (2 *N*; 5 ml) was added and the organic material removed by ether extraction. After being dried over molecular sieve for 24 hours the ether solution was concentrated by evaporation under vacuum and subjected to vapour phase chromatography; yield 30 %. See below for analysis.

b). *From (2-bromotetrafluorophenyl)lithium.* 1,2-Dibromotetrafluorobenzene (10 g) was placed in a three-necked flask cooled to —78° and an equimolar quantity of butyllithium added. After 15 minutes water (20 ml) was added and the mixture warmed to room temperature. The ether layer was removed, dried, and the products separated by vapour phase chromatography; 1-hydro-2-bromotetrafluorobenzene (3 g) was obtained as a colourless liquid. (Found: C, 31.6; H, 0.55; Br, 35.0; F, 33.3. C_6HBrF_4 calcd.: C, 31.4; H, 0.44; Br, 34.9; F, 33.2 %.)

2,2'-Bis(pentafluorophenyl)octafluorobiphenyl, $C_6F_5C_6F_4C_6F_4C_6F_5$

A mixture of 2-bromononafluorobiphenyl (5.31 g) and copper powder (8.04 g) was heated *in vacuo* in a sealed tube at 200°. After 2 days the tube was cut open and the contents washed with pentane (100 ml) and the washings discarded. The residue was extracted (Soxhlet) with ether to give a white solid; purification by vacuum sublimation at 140° gave a pure sample of 2,2'-bis(pentafluorophenyl)octafluorobiphenyl, m.p. 167–168°. Yield 1.5 g. (Found: C, 45.8; F, 54.1; mol. wt., 624. C_4F_{18} calcd.: C, 45.7; F, 54.2 %; mol. wt., 630.)

The reaction of (pentafluorophenyl)lithium with hexafluorobenzene

A sample of (pentafluorophenyl)lithium (made from 9 g of bromopentafluorobenzene) was mixed with 7.5 g of hexafluorobenzene at —78°. The stirred mixture was allowed to warm up to room temperature and left overnight; no decafluorobiphenyl was obtained on working up the reaction product. A similar reaction using methoxypentafluorobenzene in place of hexafluorobenzene produced no 2-methoxynonafluorobiphenyl.

Infrared spectra

The infrared spectra were recorded on a Grubb-Parsons double beam grating spectrophotometer; the peaks are reported in cm^{-1}.

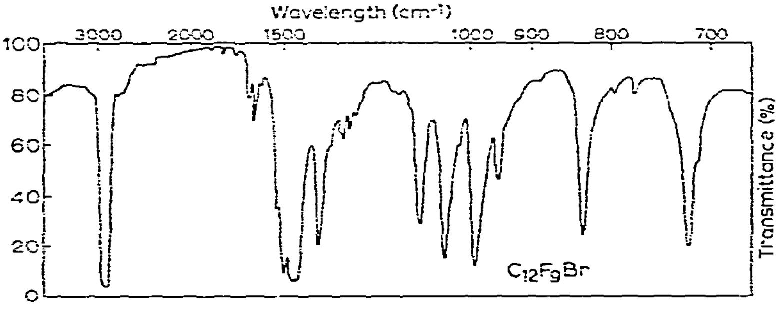


Fig. 2. Infrared spectrum of 2-bromononafluorobiphenyl in nujol mull.

$C_6F_5C_6F_4Br$ (in chloroform and carbon disulphide solutions): 1656m, 1629m, 1613wsh, 1600w, 1570vwk, 1493s, 1471s, 1445s, 1422w, 1362w, 1330vwk, 1305w, 1279w, 1263w, 1214vwk, 1148w, 1105s, 1087wsh, 1065wsh, 1048s, 1035m, 1017m, 990s, 953m, 833s, 796w, 770vwk, 759w, 720s, 711wsh.

$C_6F_5C_6F_4I$ (as above): 1656m, 1623m, 1613wsh, 1592w, 1520msh, 1506msh, 1481s, 1433s, 1366w, 1326vwk, 1299m, 1269m, 1256w, 1145w, 1098s, 1075wsh, 1064wsh, 1042s, 1033sh, 1011m, 988s, 951m, 805s, 793m, 766w, 717s, 707m.

$C_6F_5C_6F_4H$ (as above): 1656m, 1623m, 1600msh, 1541msh, 1527ssh, 1506s, 1471s, 1445s, 1397vw, 1368m, 1299m, 1282w, 1202m, 1148w, 1134vwk, 1087s, 1033m, 1022s, 1001m, 986s, 935m, 861m, 789w, 758w, 742s, 718vwk, 697s, 685w.

o-HC_6F_4Br (as above): 3067w, 1618s, 1543ssh, 1475vs, 1342w, 1333m, 1266m, 1256wsh, 1230w, 1214vwk, 1192s, 1174m, 1096s, 1087s, 1062w, 1015s, 1001s, 992s, 926w, 911w, 843s, 827s, 792w, 758w, 707s, 655w.

$(C_6F_5C_6F_4)_2Hg$ (as a mull in nujol and hexachlorobutadiene): 1653m, 1623m, 1592m, 1522s, 1497ssh, 1484s, 1466s, 1427m, 1374w, 1353m, 1297m, 1267w, 1214vwk, 1147wsh, 1136w, 1124w, 1092s, 1042s, 1018w, 990s, 947m, 919w, 862vwk, 819m, 794w, 769vwk, 717s.

$C_6F_5C_6F_4C_6F_4C_6F_5$ (as a mull in nujol and hexachlorobutadiene): 1656w, 1637m, 1603w, 1534s, 1517s, 1504s, 1497s, 1475s, 1441m, 1381vwk, 1368vwk, 1300m, 1289vwk, 1282m, 1266m, 1206vwk, 1151m, 1109s, 1075s, 1048s, 1020w, 1000m, 989s, 963m, 943w, 793w, 746s, 724s, 702s, 668vwk, 661vwk.

DISCUSSION

The infrared spectrum of 2-bromononafluorobiphenyl (I), whilst closely resembling that of decafluorobiphenyl, also shows a strong absorption at 833 cm^{-1} which we assign to the C–Br stretching frequency[9]. This peak gave us the first clue as to the identity of the material; since few other polyfluorophenyl compounds absorb in this region of the spectrum it also acts as useful fingerprint when following reactions of (I). The fact that (I) appears as one of the products from the reaction of (pentafluorophenyl)lithium and 1,2-dibromotetrafluorobenzene is strong chemical evidence that the bromine atom is in the 2-position.

Physical evidence for 2-substitution in these polyfluorobiphenyls comes from a detailed study of the H–F coupling constants in $C_6F_5C_6F_4H$ [made by hydrolysing both $C_6F_5C_6F_4Li$ and $C_6F_5C_6F_4MgBr$, which in turn are made directly from (I)]. The comparative model chosen for study was 1-hydro-2-bromotetrafluorobenzene because bromine and the pentafluorophenyl group are known to have approximately the same electronegativity[10]; if $C_6F_5C_6F_4H$ is the 2-substituted derivative, then its ^1H nuclear magnetic resonance (NMR) spectrum should be very like that of the model since the protons in the two molecules will be in virtually equivalent environments. It is evident from Fig. 3 that the two ^1H NMR spectra are indeed nearly coincident because the relevant H–F coupling constants are so close numerically, see Table.

The most striking difference between the two is that peaks in the spectrum of $C_6F_5C_6F_4H$ show a barely resolved triplet splitting (J_{H-F} = 0.7 c/sec) which is not observed in the case of the spectrum of 1-hydro-2-bromotetrafluorobenzene. This triplet is believed to arise from a long-range coupling between the proton and the 2′- and 6′-fluorine atoms in the second pentafluorophenyl ring. It would be difficult to account for such a splitting if the proton were in the 3- or 4-position as the coupling would have to extend over six, or seven, bonds. However, it has been shown previously that *ortho*-fluorine atoms in a pentafluorophenyl ring are able to couple with protons five bonds away[11], J_{H-F} in these cases lay between 0.2 and 1.1 c/sec. The ^1H NMR spectrum shown in Fig. 3 was taken using a sample of 2-hydrononafluorobiphenyl

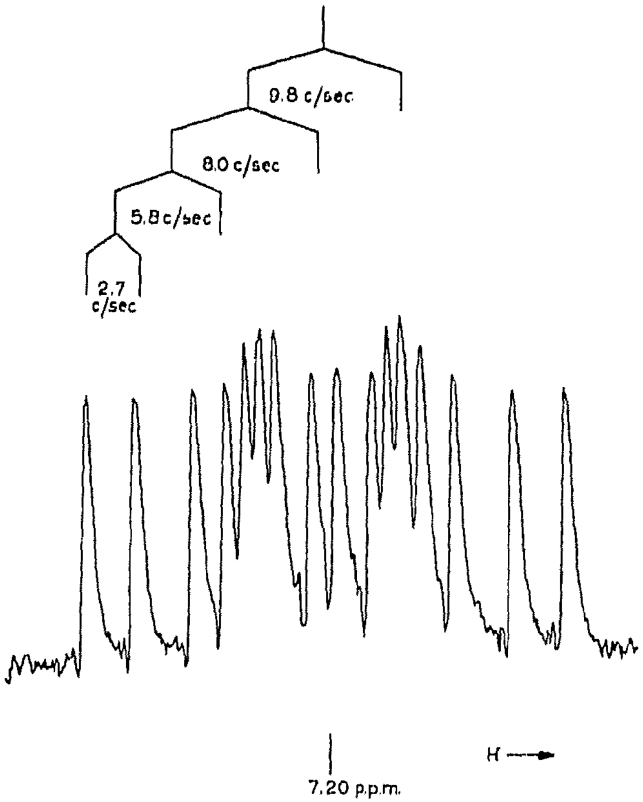


Fig. 3a. ^{1}H NMR spectrum of liquid 1-hydro-2-bromotetrafluorobenzene.

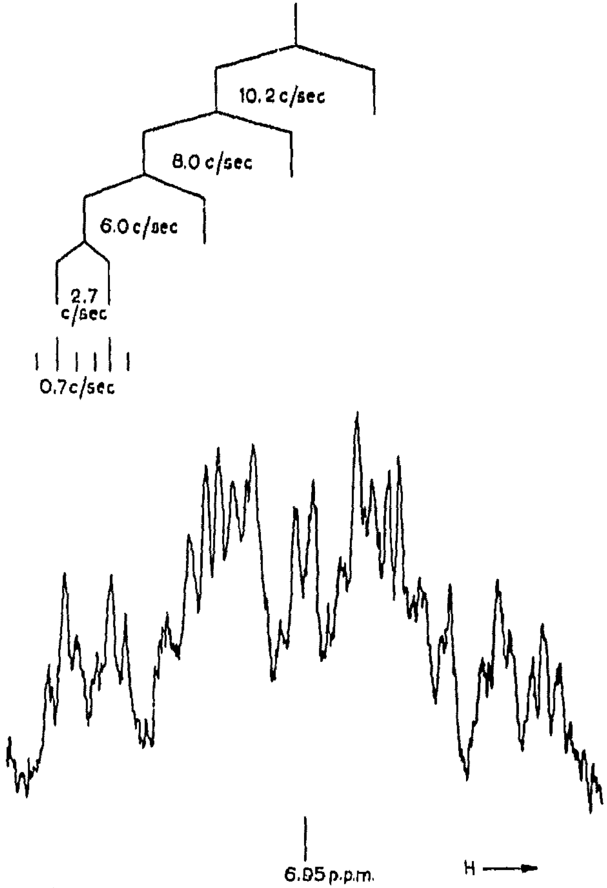
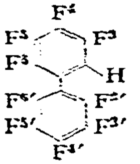
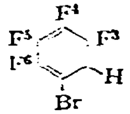


Fig. 3b. ^{1}H NMR spectrum of 2-hydrononafluorobiphenyl dissolved in CCl_3F.

TABLE I

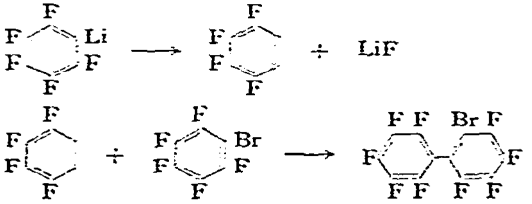
COUPLING CONSTANTS IN THE ^{1}H NMR SPECTRA OF 1-HYDRO-2-BROMOTETRAFLUOROBENZENE AND 2-HYDRONONAFLUOROBIPHENYL

	$2\text{-}HC_6F_4C_6F_5$	$1\text{-}HC_6F_4Br\text{-}2$
Chemical Shift (ppm from TMS)	6.95 ± 0.05	7.20 ± 0.05
J_{H-F^3} (c/sec)	10.3 ± 0.3	9.8 ± 0.2
J_{H-F^4} (or J_{H-F^6})	8.0 ± 0.2	8.0 ± 0.2
J_{H-F^5}	2.7 ± 0.1	2.7 ± 0.1
J_{H-F^6} (or J_{H-F^4})	6.0 ± 0.2	5.8 ± 0.1
$J_{H-F^{2'}}$ and $J_{H-F^{6'}}$	0.7 ± 0.1	—
		

dissolved in fluorotrichloromethane. There was no detectable change in the spectrum when either the concentration or the solvent was changed. However, the spectrum of the pure, super-cooled liquid was very much broader due possibly to the viscous nature of the liquid or to intermolecular hydrogen bonding.

The ^{19}F NMR spectrum of (I) dissolved in chlorotrifluoromethane shows the presence of seven magnetically different types of fluorine as expected for the 2-substituted isomer and can be understood in terms of this model. A detailed discussion of the ^{19}F NMR spectra of (I), $C_6F_5C_6F_4H$, $C_6F_5C_6F_4F$, $(C_6F_5C_6F_4)_2Hg$ and $(C_6F_5C_6F_4)_2$ will be the subject of a later paper.

When a nucleophilic reagent attacks a pentafluorophenyl compound C_6F_5X, the entering group almost always takes up the *para*-position; in no known case is the product exclusively *ortho* although it can be on rare occasions be *meta*[7]. The reaction of (pentafluorophenyl)lithium with bromopentafluorobenzene gives 2-bromononafluorobiphenyl; infrared, vapour-phase-chromatographic and ^{19}F nuclear magnetic resonance studies give no indication of the 3- or 4-substituted isomers being present even in trace amounts. This fact leads us to believe that the reaction does not take place via nucleophilic attack of C_6F_5Li on the bromopentafluorobenzene; it may well be the case that tetrafluorobenzyne is an intermediate in the reaction and that this reacts with the bromopentafluorobenzene:



a similar mechanism was postulated in the reaction of bromine with (pentafluorophenyl)lithium to account for the production of 1,2-dibromotetrafluorobenzene[8].

2-Bromononafluorobiphenyl has proved a valuable starting material for many substituted polyfluorobiphenyls since it undergoes lithium-bromine exchange with butyllithium in ether at —78° and forms a Grignard reagent in tetrahydrofuran. The presence of both these organometallic compounds was proved by hydrolysis which gave 2-hydrononafluorobiphenyl, $C_6F_5C_6F_4H$.

The usefulness of tetrahydrofuran as a medium for the preparation of (perfluoroaryl)magnesium halides is to be noted; 2-bromononafluorobiphenyl did not react with magnesium in diethyl ether solution even after continued refluxing. 1,2-Dibromotetrafluorobenzene can also be made to form a mono-Grignard reagent in tetrahydrofuran (whereas in diethyl ether the reaction is very sluggish) which on hydrolysis gives 1-hydro-2-bromotetrafluorobenzene*.

The reaction of 2-bromononafluorobiphenyl with copper powder in a sealed tube at 200° gave a fair yield of the perfluoroquaterphenyl, 2,2'-bis(pentafluorophenyl)-octafluorobiphenyl; bis(nonafluoro-2-biphenylyl)mercury, readily obtained by treating mercuric chloride in ether with (nonafluoro-2-biphenylyl)lithium, is a thermally stable white solid unaffected by air at ambient temperatures. Treatment with iodine in a sealed tube at 180° causes cleavage of both nonafluorobiphenylyl groups:

$$(C_6F_5C_6F_4)_2Hg + 2I_2 \longrightarrow 2C_6F_5C_6F_4I + HgI_2$$

The 2-iodononafluorobiphenyl produced in the reaction was synthesised independently from (pentafluorophenyl)lithium and iodopentafluorobenzene. Attempts to synthesise other 2-substituted nonafluorobiphenyls directly from the C_6F_5Li–C_6F_5X reaction have failed when $X = F$, OMe; this may be further evidence against nucleophilic attack by (pentafluorophenyl)lithium since both these compounds react with other nucleophiles to give substitution products.

Though the reaction of (pentafluorophenyl)lithium with C_6F_5X is apparently limited to the specific case of $X =$ bromine or iodine, variations of other substituents in either of the phenyl rings may produce many other useful polyfluoropolyphenyl derivatives containing functional halogen atoms; for example one can envisage terphenyl compounds by reacting together (nonafluoro-2-biphenylyl)lithium and bromopentafluorobenzene. At present we are making a thorough study of the products from the addition of (pentafluorophenyl)lithium to 1,2-bibromotetrafluorobenzene in an effort to isolate 2,2'-dibromooctafluorobiphenyl which we hope will be one of the products if the addition reaction takes place via a perfluorobenzene intermediate.

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* The formation of this Grignard reagent has been mentioned previously[8], but no details of its preparation or properties were given.

SUMMARY

The formation of 2-bromononafluorobiphenyl from (pentafluorophenyl)lithium is described. This compound can be used to prepare other 2-substituted polyfluorobiphenyls: $C_6F_5C_6F_4Li$, $C_6F_5C_6F_4MgBr$, $(C_6F_5C_6F_4)_2Hg$, $C_6F_5C_6F_4H$, $C_6F_5C_6F_4I$, and $C_6F_5C_6F_4C_6F_4C_6F_5$. The position of substitutions was checked both chemically (using the reaction of C_6F_5Li with 1,2-dibromotetrafluorobenzene) and by a study of the coupling constants in $C_6F_5C_6F_4H$ (using 1-hydro-2-bromotetrafluorobenzene as a reference compound). The ^{19}F NMR spectra of these compounds also indicate 2-substitution.

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