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PERFLUOROPHENYL DERIVATIVES OF THE ELEMENTS XIX*. REACTIONS OF SOME POLYFLUOROBENZYNE DERIVATIVES

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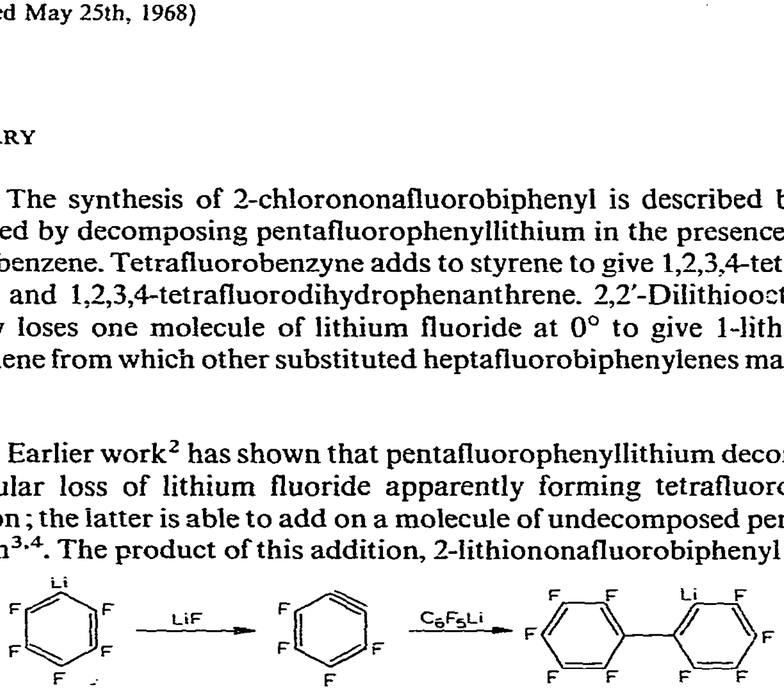
SUMMARY

The synthesis of 2-chlorononafluorobiphenyl is described but it cannot be obtained by decomposing pentafluorophenyllithium in the presence of chloropentafluorobenzene. Tetrafluorobenzyne adds to styrene to give 1,2,3,4-tetrafluorophenanthrene and 1,2,3,4-tetrafluorodihydrophenanthrene. 2,2'-Dilithiooctafluorobiphenyl readily loses one molecule of lithium fluoride at 0° to give 1-lithioheptafluorobiphenylene from which other substituted heptafluorobiphenylenes may be synthesised.

Earlier work[2] has shown that pentafluorophenyllithium decomposes by intramolecular loss of lithium fluoride apparently forming tetrafluorobenzyne in the solution; the latter is able to add on a molecule of undecomposed pentafluorophenyllithium[3,4]. The product of this addition, 2-lithiononafluorobiphenyl (I), will undergo Li/X exchange with C_6F_5X (X = H, Br or I), allowing the biphenyl group to be removed intact from further reaction; in the absence of suitable exchange material the 2-lithiononafluorobiphenyl readily decomposes by the further elimination of lithium fluoride[4]. The exchange is a remarkably efficient process when pentafluorobenzene, bromopentafluorobenzene or iodopentafluorobenzene are used as evidenced by the isolation of the biphenyl $2\text{-}XC_{12}F_9$ (X = H, Br or I, respectively) in yields approaching 70%. However, such exchange reactions are impossible when either methoxypentafluorobenzene or hexafluorobenzene is added to decomposing pentafluorophenyllithium and no 2-substituted nonafluorobiphenyl can be isolated from such systems[3].



I

To complete the series of halopentafluorobenzenes we have conducted similar experiments using chloropentafluorobenzene. Chloropentafluorobenzene undergoes lithium–chlorine exchange when treated with n-butyllithium at −78° in ether/hexane solvent as was demonstrated by the isolation of a high yield of bis(pentafluorophenyl)-

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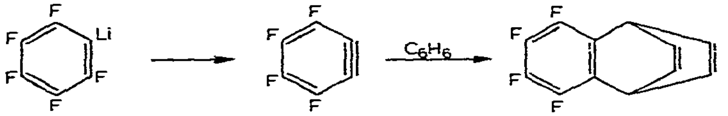
* For Part XVIII see ref. 1.

mercury on the addition of mercuric chloride to the system. However, the addition of approximately one mole of n-butyllithium to two moles of chloropentafluorobenzene at −78° followed by stirring of the mixture at room temperature for some hours failed to produce even a trace of 2-chlorononafluorobiphenyl but gave much polymeric material. This result is, presumably, due to the inability of 2-lithiononafluorobiphenyl to undergo lithium–chlorine exchange with chloropentafluorobenzene, a point verified by adding chloropentafluorobenzene to 2-lithiononafluorobiphenyl made by lithiation of 2-bromononafluorobiphenyl using n-butyllithium. 2-Chlorononafluorobiphenyl can be prepared by carefully saturating an ether/hexane solution of 2-lithiononafluorobiphenyl with chlorine gas at low temperatures; it is a thermally stable white solid, m.p. 73–74°, and readily lithiated to 2-lithiononafluorobiphenyl in ether/hexane on the addition of n-butyllithium.

There are very few pentafluorophenyl compounds which have been demonstrated to undergo exchange reactions with alkyl- or aryllithium reagents; however, one such compound is bis(pentafluorophenyl)mercury[5,6] which readily exchanges mercury for lithium when treated with n-butyllithium. We therefore carried out the decomposition of pentafluorophenyllithium in the presence of bis(pentafluorophenyl)mercury and as expected, the decomposition proceeded normally to the 2-lithiononafluorobiphenyl stage; the biphenylyllithium reagent then exchanged metal with bis(pentafluorophenyl)mercury to give good yields of bis(nonafluoro-2-biphenylyl)mercury [together with smaller quantities of (pentafluorophenyl)-(nonafluoro-2-biphenylyl)mercury] which again demonstrates the importance of Li/X exchange in the isolation of the 2-$XC_{12}F_9$ derivatives. A similar reaction should occur if dicyclopentadienylbis(pentafluorophenyl)titanium is used in place of $(C_6F_5)_2Hg$ as Stone[7] has shown that it is easily cleaved by alkyllithium reagents. This method is not the best one to employ in the synthesis of bis(nonafluoro-2-biphenylyl)-mercury due to the formation of a mixture of solid products; it is better prepared from 2-lithiononafluorobiphenyl and mercuric chloride or by heating 2-iodononafluorobiphenyl and mercury to about 200° in a vacuum:

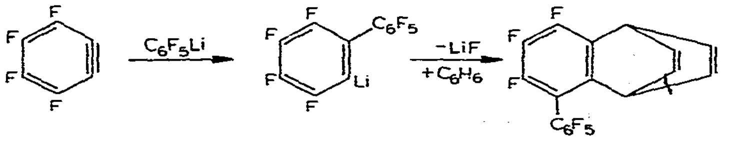
$$2\text{-}IC_{12}F_9 + Hg \xrightarrow[\text{tube}]{\text{sealed}} (2\text{-}C_{12}F_9)_2Hg + HgI_2$$

The decomposition of pentafluorophenyllithium occurs similarly in benzene, the tetrafluorobenzyne being trapped as the 1,4-addition product of benzene[8,9]:



II

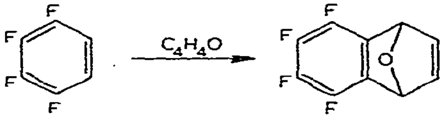
A minor, but significant side-product of this reaction is 2-lithiononafluorobiphenyl which was detected as its benzene addition compound.



III

(ratio II : III = ~ 40 : 1)

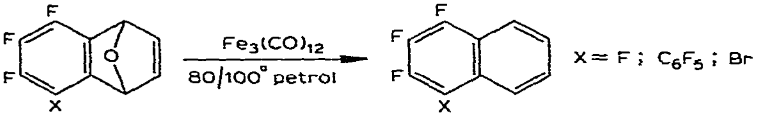
In the presence of substituted benzenes the decomposition of pentafluorophenyllithium gives mainly the tetrafluorobenzyne-1,4-addition product[8] but often we have isolated traces of 2-hydrononafluorobiphenyl, 2-bromononafluorobiphenyl and a terphenyl, $C_{18}F_{13}Br$ (identified by vapour phase chromatography and mass spectrometry) showing that the benzene addition is in competition with the addition of pentafluorophenyllithium. However, the decomposition of pentafluorophenyllithium in furan gave *only* the tetrafluorobenzyne adduct IV:



IV

indicating that furan is a better benzyne trap than benzene.

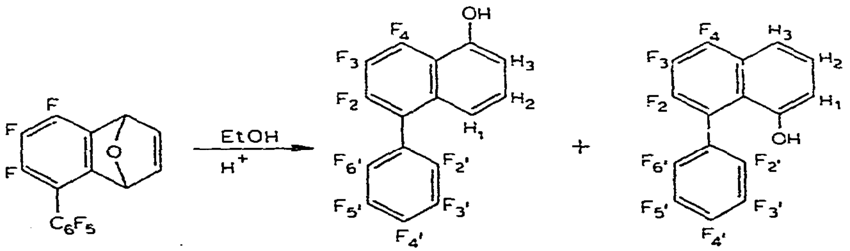
Attempts to coordinate compounds such as (IV) to iron tricarbonyl fragments failed; the main course of these reaction appeared to be the smooth removal of the oxygen atom resulting in the formation of the corresponding substituted naphthalenes:



The yield of naphthalene was lowest when X = Br, possibly due to secondary reactions involving attack on the bromine atom.

The addition of furan or benzene to decomposing 1-lithio-2-bromotetrafluorobenzene shows, in agreement with our earlier studies[10], that this lithium reagent produces mainly trifluorobromobenzyne but with a detectable amount (1–5%) of tetrafluorobenzyne formed by loss of lithium bromide; Heaney and co-workers have recently reported similar results[8].

Treatment of 1-(pentafluorophenyl)-2,3,4-trifluoro-5,8-epoxy-5,8-dihydronaphthalene (V) with ethanolic hydrochloric acid converted it into a mixture of products, the three major components of which were separated by thin layer chromatography; two of these were identified as the isomeric naphthols (VI) and (VII) (the third, which analysed as another isomer of (V) but one apparently having no hydroxyl group, was not investigated further):



V VI VII

The ^1H NMR spectrum of (VII) at 100 Mc shows two groups of lines in the aromatic region, relative intensities 1:2. The first group, a triplet, is due to $H_2[J(H_2–H_1) =$

$J(H_2–H_3) = 8.2$ cps]; the other group is a second-order multiplet due to an overlap of peaks arising from H_1 and H_3. At 220 Mc this multiplet becomes simplified to two doublets of equal intensity, that due to H_3 being considerably broadened by coupling to F_4 ($J = 1.8$ cps); the *meta* coupling $J(H_1–H_3)$ is too small to be identified. The ^{19}F NMR spectrum of (VII) shows the expected six groups of lines of intensities 1:1:2:1: 2:1 (field increasing) due, respectively, to F_2, F_4, $F_{2'}+F_{6'}$, $F_{4'}$, $F_{3'}+F_{5'}$, F_3. The coupling constants are within the general range found in fluoroaromatic compounds except that the *meta* coupling $J(F_2–F_4)$ is rather large, 10 cps. The following points of interest arise from a study of the spectrum:

(*i*) the expected doublet of doublets for F_2 is further split into triplets by $F_{2'}$ and $F_{6'}$ ($J = 3.6$ cps);

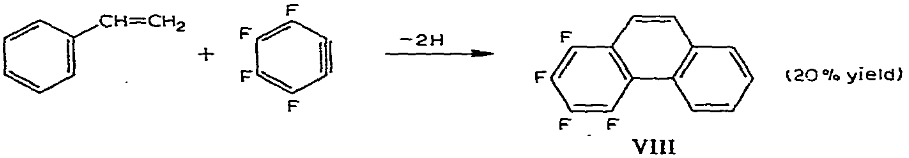
(*ii*) the (through space?) coupling between F_4 and H_3 ($J = 1.8$ cps) splits the expected doublet of doublets for F_4 into an eight-line multiplet; this coupling, not possible in isomer (VI), is conclusive proof for the identification of this isomer as (VII).

The isomer (VI) has a more simple ^1H spectrum, the expected three groups of lines of equal intensities being observed at both 100 and 220 Mc. The group assigned to H_1, a doublet of triplets [$J(H_1–H_2) = 8.0$, $J = 1.1$ cps], collapses to a doublet of doublets on decoupling at frequency H_3; the group assigned to H_3, a doublet [$J(H_3–H_2) = 8.0$ cps] of rather broad lines, becomes sharper on decoupling at frequency H_1. Thus the triplet splitting on H_1 is caused by two couplings of equal magnitude (1.1 cps) one of which is $J(H_1–H_3)$, the other presumably between H_1 and a fluorine atom. The ^{19}F NMR spectrum had six groups of lines, intensities 1:2:1:1:1:2 assigned to F_2, $F_{2'}+F_{6'}$, F_4, $F_{4'}$, F_3, $F_{3'}+F_{5'}$; the *meta* coupling $J(F_2–F_4)$ was again rather large, 8.0 cps. Points of interest in this spectrum were:

(*i*) the peak due to F_4 was a simple doublet of doublets as no coupling to the OH group was possible;

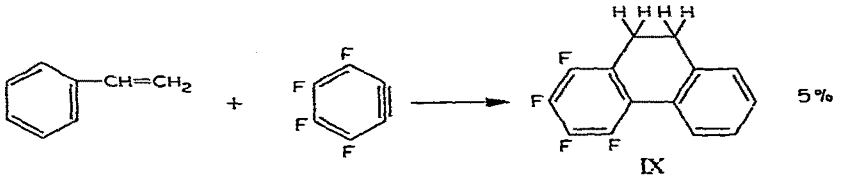
(*ii*) the expected doublet of doublets for F_2 was further split into a triplet ($J = 3.5$ cps) by $F_{2'}$ and $F_{6'}$ and split yet again by $F_{4'}$ into a doublet; similarly, the peak due to $F_{4'}$ (expected to be a triplet of triplets from coupling to $F_{3'}F_{5'}$ and $F_{2'}F_{6'}$) was further split to doublets by F_2 as was checked by decoupling experiments in which the sample was irradiated by frequency F_2; under these conditions the $F_{4'}$ resonance collapsed to a triplet of triplets.

As part of a study on the synthesis of metal carbonyl adducts derived from (II) but having several of the hydrogen atoms substituted by other groups, we allowed pentafluorophenyllithium to decompose in the presence of a large excess of styrene.



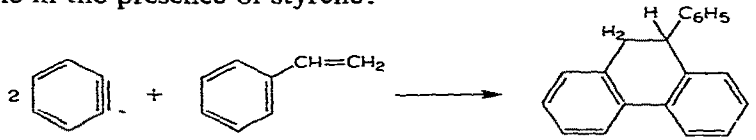
VIII

In this case, however, the addition of styrene to tetrafluorobenzyne occurred in a different manner to give the tetrafluorophenanthrene (VIII). For such a product to be isolated there must have been formed the intermediate dihydrophenanthrene derivative which we presume to have been dehydrogenated by tetrafluorobenzyne or by LiH elimination; on looking more closely at the reaction products we were able to obtain rather small quantities of this intermediate:



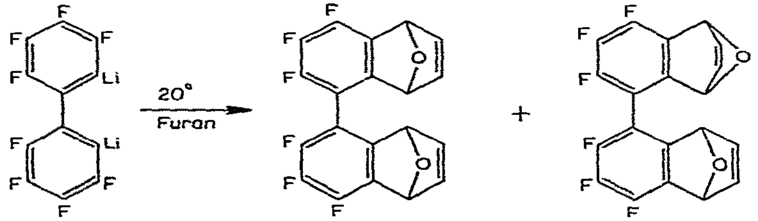
IX

On heating (IX) with sulphur it was possible to convert it completely into (VIII) with the parallel formation of hydrogen sulphide. The ultraviolet spectrum of (VIII) is very similar to that of normal phenanthrene: the mass spectrum had a parent ion at $m/e = 250$ whilst the NMR spectra at 220 and 100 Mc (^{1}H and ^{19}F) though complex, were in agreement with the formulation. The mass spectrum of (IX) was similar except it had a peak at $m/e = 252$ representing the parent ion and two relatively strong peaks of approximately equal height at $m/e = 251$ and 250 (mainly due to loss of the two reactive hydrogen atoms in the $-CH_2CH_2-$ bridge?); the loss of aromatic protons from (VIII) and (IX) gave only very minor peaks throughout their mass spectra. This behaviour of tetrafluorobenzyne is different to that shown by normal benzyne in the presence of styrene:



Tetrafluorophenanthrene does not react with triiron dodecacarbonyl in refluxing 80–100° petrol ether.

The decomposition of 2,2'-dilithiooctafluorobiphenyl has proved to be very interesting. In furan the loss of two moles of lithium fluoride gave a high yield of white solid which analysed as the expected difuran adduct. The ^{19}F NMR spectrum of a sample dissolved in tetrahydrofuran showed that two isomers of the di-adduct were present:



X XI

Isomer (X) showed 3 groups of lines in the ^{19}F NMR spectrum whereas in (XI) the fluorine atoms of each ring are in differing environments and give rise to six groups of lines.

During attempts to synthesise 2,2'-dichlorooctafluorobiphenyl by lithium–chlorine exchange between 2,2'-dilithiooctafluorobiphenyl and chloropentafluorobenzene, small quantities of a pale yellow solid analysing as $C_{12}F_7H$ were obtained on working up the reaction mixture, but no 2,2'-dichlorooctafluorobiphenyl could be detected* (this dichloride has subsequently been synthesised by the action of chlorine

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* The corresponding Li/I exchange occurs readily in the presence of iodopentafluorobenzene to give high yields of 2,2'-diiodooctafluorobiphenyl.

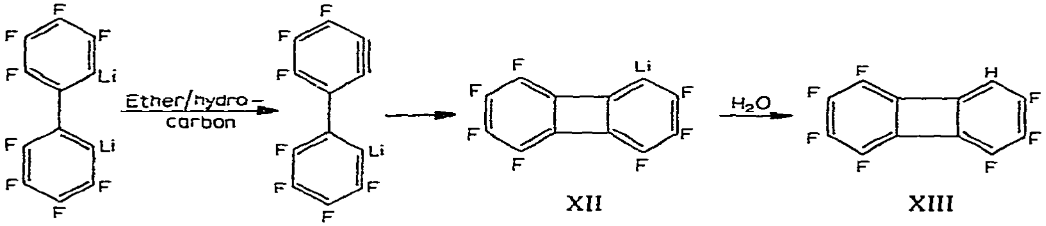
TABLE 1

^{19}F CHEMICAL SHIFTS[a] AND SPIN-SPIN COUPLING CONSTANTS[b] OF THE FURAN ADDUCTS DERIVED FROM 2,2'-DILITHIOOCTAFLUOROBIPHENYL

No.	$\delta(F_4,F_{4'})$	$\delta(F_5,F_{5'})$	$\delta(F_6,F_{6'})$	J_{4-5}	J_{4-6}	J_{5-6}	J_{6-H}
(X)	140.9	163.0	140.0	17.5	5.0	22.0	2.7
(XI)	139.0	162.8	139.3	17.3	5.0	21.9	2.7
	140.4	163.1	139.6				

[a] In tetrahydrofuran, ±0.1 ppm relative to CF_3Cl_3. [b] ±0.1 cps.

on 2,2'-dilithiooctafluorophenyl[11]). The solid was later identified as 2,3,4,5,6,7,8-heptafluorobiphenylene (referred to below as 1-hydroheptafluorobiphenylene, XIII) which is presumably the hydrolysis product of (XII); this lithium salt could arise from 2,2'-dilithiooctafluorobiphenyl via initial loss of one mole of lithium fluoride and followed by addition of the intact half of the molecule to the benzyne intermediate thus created:



XII XIII

1-Hydroheptafluorobiphenylene has, as the parent ion in the mass spectrum, a strong peak at $m/e = 278$ and, significantly, one at 277 (*i.e.* loss of the hydrogen atom from the parent ion). Meta-stable peaks corresponding to the reactions,

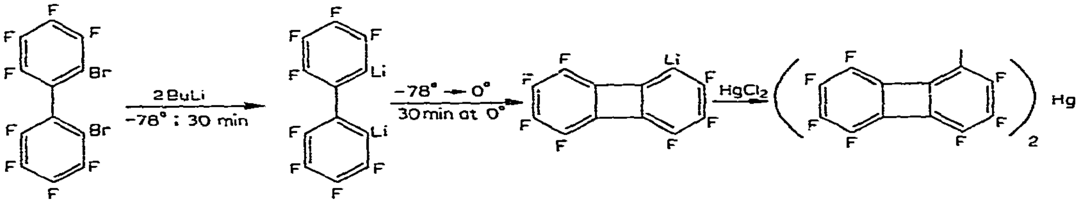
$$C_{12}F_7H \xrightarrow{-CF} C_{11}F_6H$$

$$C_{12}F_7H \xrightarrow{-CF_2} C_{11}F_5H$$

$$C_{12}F_7H \xrightarrow{-CF_3} C_{11}F_4H$$

gave further proof as to the correctness of the molecular formula. The compound consistently gave good analyses for hydrogen and exhibited a proton NMR spectrum centred at 6.52 ppm from tetramethylsilane; this consisted of four rather broad lines due to coupling of the hydrogen to the single fluorine atoms *ortho*, *meta* and *para* to it. The broadness of the lines may be due to some cross-ring H–F coupling. The ^{19}F NMR of XIII showed six groups of lines having intensity ratios 1:1:2:1:1:1 the group of intensity two arising from overlap of two of the absorptions (this was verified by recording the spectrum of 1-bromoheptafluorobiphenylene, see below, when this overlap did not occur and the expected seven equally intense lines could all be resolved).

By allowing about 1.5–2 g of pure 2,2'-dilithiooctafluorobiphenyl to remain at 0° for thirty min before hydrolysing the decomposition mixture, it was possible to isolate about a 30% yield of 1-hydroheptafluorobiphenylene; addition of bromine instead of water gave pale yellow crystals of 1-bromoheptafluorobiphenylene. It appears to be unnecessary to isolate either 1-hydroheptafluorobiphenylene or 1-bromoheptafluorobiphenylene in order to synthesise perfluorobiphenylenylmetal derivatives. The following synthetic route, carried out for bis(heptafluoro-1-biphenylenyl)mercury, is far simpler and much less time consuming:



It is apparent from this biphenylene formation that 1-lithioheptafluorobiphenylene is far more thermally stable than 2,2'-dilithiooctafluorobiphenyl.

EXPERIMENTAL

Reactions were carried out under an atmosphere of dry, oxygen-free nitrogen. Analyses were carried out by Dr. A Bernhardt, Mülheim, Ruhr and by the microanalytical department at Queen Mary College. We thank the Imperial Smelting Corp. Ltd., for gifts of bromopentafluorobenzene, iodopentafluorobenzene and 1,2-dibromotetrafluorobenzene and the Imperial Chemical Industries Ltd, for a sample of chloropentafluorobenzene. The syntheses of 2-bromononafluorobiphenyl[3] and 2,2'-dibromooctafluorobiphenyl[10,11] have been described previously by us.

Lithiation of chloropentafluorobenzene

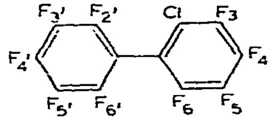
Chloropentafluorobenzene (5.06 g) and n-butyllithium (one molar quantity) were mixed in ether (75 ml) at −78° and stirred for one h. Mercuric chloride (3.39 g) was then added and the mixture allowed to warm up to room temperature; filtration, evaporation of the solvent and vacuum sublimation gave bis(pentafluorophenyl)-mercury (85%) identified by IR and m.p.

Reactions of pentafluorophenyllithium with chloropentafluorobenzene

Chloropentafluorobenzene (10.12 g) and n-butyllithium (0.5 molar equivalent) were mixed in 75 ml of ether at −78°. After one h the mixture was allowed to remain at room temperature for 14 h. On hydrolysis and work-up of the products, no 2-chlorononafluorobiphenyl could be detected in the polymeric solid.

Preparation of 2-chlorononafluorobiphenyl

2-Bromononafluorobiphenyl (5 g) in 75 ml of ether was treated with n-butyllithium (one molar equiv.) at −78°; after 5 min the solution was saturated with chlorine gas. Evaporation of the solvent followed by vacuum sublimation gave 2-chlorononafluorobiphenyl, m.p. 73–74°, as a white solid. Yield: 80%. (Found: C, 41.2; H, 0.08; F, 48.9. $C_{12}ClF_9$ calcd.: C, 41.1; H, 0.00; F, 49.1%.)



The ^{19}F NMR chemical shifts of 2-chlorononafluorobiphenyl dissolved in carbon tetrachloride were (relative to $CFCl_3$): $F_{2'}$ and $F_{6'}$, 138.4, $F_{3'}$ and $F_{5'}$ 161.0, $F_{4'}$ 150.7, F_5 157.35, F_4 150.3, and F_3 and F_6 135–136 ppm. The chemical shifts of the F_3 and F_6 atoms are within the prediction of 135.5 ± 0.5 ppm made by Schaefer, Hruska and Hutton[12].

Reaction of 2-lithiononafluorobiphenyl with chloropentafluorobenzene

2-Lithiononafluorobiphenyl, synthesised as above, was allowed to stand at −78° in the presence of chloropentafluorobenzene; hydrolysis of the reaction mixture followed by vacuum sublimation gave only 2-hydrononafluorobiphenyl (90%), m.p. 42–43°.

Reaction of 2-chlorononafluorobiphenyl with n-butyllithium

2-Chlorononafluorobiphenyl (1.1 g) in 50 ml of ether was mixed with a molar equiv. of n-butyllithium at −78°. After one h, the mixture was hydrolysed (still at −78°); work-up followed by vacuum sublimation gave 2-hydrononafluorobiphenyl (90%).

Reaction of bis(pentafluorophenyl)mercury with n-butyllithium

Bis(pentafluorophenyl)mercury was partially lithiated at −78° to pentafluorophenyllithium by the addition of 0.5 molar equiv. of n-butyllithium; the reaction mixture was then stirred for 14 h at room temperature. Filtration of the solution, evaporation of the solvent followed by vacuum sublimation at 140–160° gave bis(2-nonafluorobiphenylyl)mercury (identified by m.p., mixed m.p. and IR spectrum); 40%. The sublimate obtained at 100° appeared, from its IR spectrum to be mainly pentafluorophenyl(2-nonafluorobiphenylyl)mercury.

Reaction of 2-iodononafluorobiphenyl with mercury

2-Iodononafluorobiphenyl, prepared by adding iodine to 2-lithiononafluorobiphenyl, was heated with mercury in a sealed pyrex tube at 240° for 20 h when a 33% yield of bis(2-nonafluorobiphenylyl)mercury was obtained.

Decomposition of pentafluorophenyllithium in presence of styrene

Pentafluorophenyllithium, prepared in ether (100 ml) from bromopentafluorobenzene (8 g) and n-butyllithium, and styrene (25 ml) were stirred at room temperature for 14 h. The solution was filtered to remove lithium fluoride and the solvent evaporated off on a water pump to yield a white solid. Recrystallization of this solid from ethanol gave (VIII), m.p. 171–172°, in 20% yield. (Found: C, 67.0; H, 2.5; F, 29.5. $C_{14}H_6F_4$ calcd.: C, 67.2; H, 2.4; F, 30.4%.) The mass spectrum confirmed the mol.wt. as 250.

Removal of the ethanol from the above mother liquor followed by recrystallization from n-butanol gave (IX), m.p. 71–72°, in 5% yield. (Found: C, 66.2; H, 3.0. $C_{14}H_8F_4$ calcd.: C, 66.7; H, 3.2%.) The mass spectrum indicated a mol.wt. of 252.

Reaction of IX with sulphur

(IX), 0.2 g, was heated in a sealed pyrex tube with 0.2 g of sulphur to 210° for 36 h. Extraction and recrystallization of the product from pentane gave (VIII), m.p.

170–171°, in virtually quantitative yield; hydrogen sulphide appeared, by smell, to be the other product.

Decomposition of pentafluorophenyllithium in benzene

Pentafluorophenyllithium, from bromopentafluorobenzene (8 g, 32.4 mmoles) and n-butyllithium (32.4 mmoles), was allowed to decompose in 200 ml of benzene for 18 h at room temperature. Work-up and sublimation at 60° gave 1,2,3,4-tetrafluorobenzobicyclo[2,2,2]octatriene (5.6 g, 75%), m.p. 73–74°. (Found: C, 63.6; H, 2.6; F, 33.8; mol.wt. osmometric in benzene, 239. $C_{12}H_6F_4$ calcd.: C, 63.7; H, 2.7; F, 33.6%; mol.wt., 226.)

Further sublimation at 100° gave 1-pentafluorophenyl-2,3,4-trifluorobenzobicyclo[2,2,2]octatriene (0.26 g, 2%) m.p. 171–173°. (Found: C, 57.8; H, 1.6; F, 40.6; mol.wt. osmometric in $CHCl_3$, 383. $C_{18}H_6F_8$ calcd.: C, 57.8; H, 1.6; F, 40.7%; mol.wt., 374.)

Ratio $C_{12}H_6F_4$:$C_{18}H_6F_8$=37.5:1. The latter compound can be made in 60% yield by allowing 2-lithiononafluorobiphenyl to decompose at room temperature in benzene solution.

Decomposition of pentafluorophenyllithium in furan

Pentafluorophenyllithium, from bromopentafluorobenzene (12.35 g, 50 mmoles) and n-butyllithium (50 mmoles), ether (50 ml) and freshly distilled furan (100 ml) were stirred at room temperature for 18 h. Filtration, evaporation of the solvents and sublimation at 50° gave 1,2,3,4-tetrafluoro-5,8-epoxy-5,8-dihydronaphthalene (7.9 g, 73%), m.p. 56.5–58° (literature value[2]: 56–57°). Further sublimation at 100°, or GLC analysis failed to detect the presence of any 1-pentafluorophenyl-2,3,4-trifluoro-5,8-epoxy-5,8-dihydronaphthalene (made in 59% yield by decomposing 2-lithiononafluorobiphenyl in furan, m.p. 137.5–139°).

Reaction of furan-adducts with iron carbonyls

1,2,3,4-Tetrafluoro-5,8-epoxy-5,8-dihydronaphthalene (0.324 g, 1.5 mmoles) and triiron dodecacarbonyl (0.252 g, 0.5 mmoles) were sealed into a pyrex tube containing 1 ml of 100/120° petrol ether and heated at 90° for 3 h. Extraction of the tube with 40/60° petrol ether gave 1,2,3,4-tetrafluoronaphthalene (0.18 g, 60%) m.p. 106–107° (identified by comparison of its IR spectrum with that of an authentic sample).

Using iron pentacarbonyl gave the naphthalene in 40% yield.

The other furan adducts reacted in a similar fashion.

1-Pentafluorophenyl-2,3,4-trifluoro-5,8-epoxy-5,8-dihydronaphthalene was also converted into 1-pentafluorophenyl-2,3,4-trifluoronaphthalene (73%) by hydrogenation using Raney nickel (2 days) followed by dehydration using a refluxing glacial acetic acid/hydrobromic acid mixture.

Conversion of 1*-pentafluorophenyl-*2,3,4*-trifluoro-*5,8*-epoxy-*5,8*-dihydronaphthalene to isomeric naphthols*

1-Pentafluorophenyl-2,3,4-trifluoro-5,8-epoxy-5,8-dihydrononaphthalene (0.8 g) was dissolved in ethanol (30 ml) and conc. hydrochloric acid (30 ml) and the mixture refluxed for 24 h. Addition of water (100 ml) gave a white precipitate which was extracted with ether (2 x 50 ml). Drying of the ether ($MgSO_4$), evaporation to dryness followed by thin layer chromatography on Kieselguhr HF254 using 60/80° petrol ether/acetone (90 : 10) as eluent, gave at least 6 bands of which the major three were extracted, examined by ^1H and ^{19}F NMR and found to be:

(*a*) 1-Pentafluorophenyl-2,3,4-trifluoro-5-naphthol (0.27 g, 34%), m.p. 171–173°. (Found: C, 53.1; H, 1.1; F, 41.8. $C_{16}H_4F_8O$ calcd.: C, 52.8; H, 1.1; F, 41.7%.)

(*b*) 1-Pentafluorophenyl-2,3,4-trifluoro-8-naphthol (0.08 g, 10%), m.p. 110.5–111.5°. (Found: C, 52.9; H, 1.3. $C_{16}H_4F_8O$, calcd.: C, 52.8; H, 1.1%.)

(*c*) A white solid apparently isomeric with the above naphthols but which did not have an O–H vibration in the IR spectrum (0.11 g, 13%), m.p. 131.5–133.5°. (Found: C, 53.2; H, 0.8; F, 41.7. $C_{16}H_4F_8O$ calcd.: C, 52.8; H, 1.1; F, 41.7%.)

Reaction of 2,2'-dilithiooctafluorobiphenyl with halopentafluorobenzenes

(*a*) *C_6F_5I.* 2,2'-Dibromooctafluorobiphenyl after lithiation at −78° in ether by n-butyllithium was treated with a slight excess of iodopentafluorobenzene (at −78°) and the mixture stirred for 1.5 h; water was then added and the products worked up to give a high yield (*ca.* 90%) of 2,2'-diiodooctafluorobiphenyl (identity checked with an authentic specimen). Other products identified (GLC) but not isolated were pentafluorobenzene (from hydrolysis of pentafluorophenyllithium) and 2-hydro-2'-iodooctafluorobiphenyl.

(*b*) *C_6F_5Cl.* 2,2'-Dilithiooctafluorobiphenyl (from 2,2'-dibromooctafluorobiphenyl, 3.32 g) and chloropentafluorobenzene (2 ml) were stirred at −78° for 2 h; hydrolysis yielded only 2,2'-dihydrooctafluorobiphenyl (2.2 g, 100%). When the same reaction was attempted at 0° for 0.5 h the mixture showed considerable darkening; hydrolysis and work-up produced unreacted chloropentafluorobenzene, small quantities of 2,2'-dihydrooctafluorobiphenyl and (as the major isolable component) 1-hydroheptafluorobiphenylene (see below).

Decomposition of 2,2'-dilithiooctafluorobiphenyl in the presence of furan

2,2'-Dilithiooctafluorobiphenyl (from 2,2'-dibromooctafluorobiphenyl, 1.854 g) in ether (75 ml) was stirred with 50 ml of freshly distilled furan for 0.5 h at −78°; the mixture was then warmed to room temperature and stirred for some hours. Filtration, removal of the solvents and vacuum sublimation at 150–170° (10^{-4} mm) gave the difuran adduct as a white solid, m.p. 204–208.5°; 0.52 g, 32%. (Found: C, 60.7; H, 2.1. $C_{20}H_8F_6O_2$ calcd.: C, 60.9; H, 2.0%.) ^{19}F NMR demonstrated the presence of two isomers (see Table 1).

Decomposition of 2,2'-dilithiooctafluorobiphenyl at 0°

(*i*) *Followed by the addition of water.* n-Butyllithium (6 ml of 1.56 molar hexane solution) was added to 2,2'-dibromooctafluorobiphenyl (2 g) in ether (100 ml) at −78° and stirred for half-an-hour; the mixture was warmed to 0° and stirred for a further half-an-hour, being considerably darkened after this period. Water (75 ml) was added and the mixture stirred at room temperature for 4 h. The dark-brown organic layer was separated, dried ($MgSO_4$) and filtered; removal of solvent gave a dark-brown oil; analytical GLC indicated the presence of one main component eluting shortly after 2,2'-dihydrooctafluorobiphenyl (which was present in trace amounts). Vacuum sublimation of the oil, 60–80° (10^{-4} mm) followed by recrystallisation from ethanol, gave a light-yellow solid, m.p. 81–83.5° (Found: C, 51.9; H, 0.5, 0.45; F, 47.6; mol. wt.

mass spectrum, 278. $C_{12}HF_7$ calcd.: C, 51.8; H, 0.4; F, 47.8%; mol.wt., 278.)

The ^{19}F NMR spectrum showed seven groups of lines at 130.8, 137.1, 140.8, 141.0, 150.4, 151.2 and 156.6 ppm relative to $CFCl_3$ in the ratio 1 : 1 : 1 : 1 : 1 : 1 : 1.

(*ii*) *Followed by the addition of bromine.* 2,2′-Dilithiooctafluorobiphenyl (from 2,2′-dibromooctafluorobiphenyl, 1.33 g) was allowed to react as above, but bromine (0.5 ml) was added at 0° in lieu of water. The resultant mixture was stirred at room temperature for 18 h and then stirred with potassium thiosulphate solution to remove unreacted bromine. The organic layer was separated, dried ($MgSO_4$) and filtered; removal of the solvent gave a dark-brown viscous oil. Vacuum sublimation, 80–100° (10^{-4} mm) followed by recrystallisation from ethanol gave light-yellow needles, m.p. 65–68°; yield 0.24 g (23%). (Found: C, 39.7; H, 0.0. $C_{12}BrF_7$ calcd.: C, 40.4; H, 0.0%.)

The ^{19}F NMR spectrum showed seven groups of lines at 124.8, 137.1, 137.8, 139.9, 149.2, 149.9 and 151.7 ppm relative to $CFCl_3$ in the ratio 1 : 1 : 1 : 1 : 1 : 1 : 1.

(*iii*) *Followed by the addition of mercuric chloride.* The above procedure was repeated using 2,2′-dibromooctafluorobiphenyl (2.17 g) except that mercuric chloride (0.65 g) was added at 0°. The mixture was stirred for 60 h at room temperature and the orange-brown ether solution filtered off from the precipitate of lithium chloride and unreacted mercuric chloride.

Removal of solvent from the solution followed by addition of ethanol gave a yellow solid which sublimed at 160–170° (10^{-4} mm) to a light-yellow solid, m.p. 237–239°; yield 0.19 g (11% overall). (Found: C, 38.3; H, 0.0; F, 35.4. $C_{24}F_{14}Hg$ calcd.: C, 38.2; H, 0.0; F, 35.2%.)

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Note added in proof. 1-Lithioheptafluorobiphenylene apparently forms no furan adduct when stirred in furan solution for several hours at room temperature; only its hydrolysis product XIII was isolated on working up the reaction mixture. This high thermal stability is presumably a chemical reflection of the non-aromatic nature of the biphenylene system which will not allow the decomposition of XII to proceed via a benzyne-type intermediate.