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AROMATIC POLYFLUORO COMPOUNDS—XXVIII[1]

FURTHER REACTIONS OF THE PENTAFLUOROPHENYL ANION

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Abstract—The pentafluorophenyl anion from pentafluorophenyllithium has been used as a nucleophile and as a source of tetrafluorobenzyne. As a nucleophile it was used to make polyfluorobi- and -terphenyl derivatives from perfluorotoluene, perfluoro-*o*-xylene, pentafluoronitrobenzene and bromopentafluorobenzene, and polyfluoropolyaryls from perfluorobiphenyl. It also attacked decafluorocyclohexene and chlorotrifluoroethylene presumably, by an addition-elimination sequence. Reactions using the tetrafluorobenzyne intermediate were carried out in the presence of excess bromopentafluorobenzene, pentafluorobenzene and various lithium halides, in some cases with variation of the solvent. A mechanism for some of these reactions is postulated.

Pentafluorophenyl-Lithium, previously prepared by two methods is a useful precursor in the synthesis of pentafluorophenyl derivatives.[2] Also, at temperatures above 0° it decomposes to give a tetrafluorobenzyne intermediate. Further reactions of the pentafluorophenyl anion used both as a nucleophile and as a source of tetrafluorobenzyne are now described.

In three recent communications[3–5] similar reactions have been reported. The chemistry of 2-bromo-nonafluorobiphenyl, observed[3] during attempts to prepare pentafluorophenyl derivatives of metals using pentafluorophenyl-lithium in ether–hexane mixtures, was investigated and its structure indicated by F^{19} NMR. A tentative mechansim for the reactions involved was based on the formation of tetrafluorobenzyne.

In our work the reaction of pentafluorophenyl-lithium with excess of bromopentafluorobenzene was first carried out at −40° in ether. A pale yellow ether insoluble fraction, which was mainly organic and contained Br and F, and probably a mixture of poly-phenyls, $C_6F_5(C_6F_4)_nBr$ was obtained together with an ether soluble fraction shown by gas chromatography to contain three components. Separation using preparative gas chromatography gave 1,2-dibromotetrafluorobenzene, 2-bromononafluorobiphenyl and 4-bromononafluorobiphenyl in the ratio of 1:1:8. The structures of these three compounds were proved unambiguously. The dibromotetrafluorobenzene was identical to that prepared by bromination of 1,2,3,4-tetrafluorobenzene[6] and the bromononafluorobiphenyls were synthesized independently.

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[1] Part XXVII, *J. Chem. Soc.* 6329 (1965).

[2] P. L. Coe, R. Stephens and J. C. Tatlow, *J. Chem. Soc.* 3727 (1962).

[3] D. E. Fenton, A. J. Park, A. G. Massey and D. Shaw, *Tetrahedron letters* **16**, 449 (1964).

[4] D. E. Fenton, A. J. Park, A. G. Massey and D. Shaw, *J. Organometallic Chem.* **2**, 437 (1964).

[5] N. N. Vorozhtsov Jr., V. A. Barkharsh, N. G. Iranova and A K. Petrov, *Tetrahedron letters* **47**, 3575 (1964).

[6] M. Hellman, A. J. Bilbo and W. H. Pummer, *J. Amer. Chem. Soc.* **77**, 3650 (1955).

The 2-bromo isomer resulted from a crossed Ullmann reaction between bromopentafluorobenzene and 1,2-dibromotetrafluorobenzene. This reaction gave the three expected products, perfluorobiphenyl[7], 2,2′-dibromooctafluorobiphenyl and 2-bromononafluorobiphenyl. 4-Bromononafluorobiphenyl was obtained from 4-hydrazino-nonafluorobiphenyl (of known orientation[8]) and bromine. The samples of 2- and 4-bromononafluorobiphenyl were identical to the products of the reaction between pentafluorophenyl-lithium and bromopentafluorobenzene. The 4-bromo compound is the expected product from a nucleophilic displacement reaction of $C_6F_5^{(-)}$ and bromopentafluorobenzene, which is substituted mainly in the position *para* to the bromine atom[9]. In an analogous manner the polyphenyls obtained come from nucleophilic attack on polyfluorobromobiphenyls which are known to be very susceptible to nucleophilic attack[8] and are substituted in position 4. The 2-bromo isomer would arise from decomposition of some pentafluorophenyl anion to the tetrafluorobenzyne intermediate, addition to this intermediate of unchanged pentafluorophenyl anion to give 2,2′,3,3′,4,4′,5,5′,6-nonafluorobiphenyl-lithium, followed by halogen metal interchange with excess bromopentafluorobenzene to give the observed product. Evidence for this type of mechanism has been found in the case of 2-bromophenyl-lithium when the product isolated was 2,2′-dibromobiphenyl.[10] Also, 2-lithiononafluorobiphenyl has been prepared from 2-bromononafluorobiphenyl and n-butyl-lithium and treated with iodopentafluorobenzene. The major product obtained was 2-iodononafluorobiphenyl, indicating that halogen metal interchange in this series does in fact take place. Further, we have evidence from gas chromatography that a small amount of 2,H-nonafluorobiphenyl could be present in the crude product. This would be expected if any of the 2-lithioderivative survived until the work up. From other experiments we and other workers[11] have evidence that 2-lithiononafluorobiphenyl is formed, since addition of water to a solution of pentafluorophenyl-lithium free from lithium halides gives only 2H-nonafluorobiphenyl. Further indication of the halogen metal interchange comes from the fact that in the absence of excess bromopentafluorobenzene the yields of the biphenyls are very small even if a large excess of n-butyl bromide is present. It is of course well known that the equilibrium

$$nC_4H_9Li + ArBr \rightleftharpoons ArLi + nC_4H_9Br$$

is well to the right so that excess n-butylbromide would be expected to have little effect.

The 1,2-dibromotetrafluorobenzene seems to arise from addition of lithium bromide to tetrafluorobenzyne followed by halogen metal interchange. Pentafluorophenyl-lithium is reasonably stable below −20°[2] but since benzyne formation takes place at higher temperatures, at 15° the proportions of 1,2-dibromotetrafluorobenzene: 2-bromononafluorobiphenyl: 4-bromononafluorobiphenyl were 40:10:1. Thus, the products arising from the benzyne were increased at the expense of nucleophilic attack. Also the amount of polymer formed was negligible whereas at low temperature:

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[7] E. Nield, R. Stephens and J. C. Tatlow, *J. Chem. Soc.* 166 (1959).

[8] J. Burdon, I. Farazmand and J. C. Tatlow, unpublished results.

[9] J. Burdon, P. L. Coe and C. R. Marsh, to be published.

[10] H. Gilman and B. J. Gay *J. Org. Chem.* 22, 447 (1957).

[11] A. G. Massey and D. E. Fenton, *Tetrahedron* 21, 3009 (1965).

it is the major product. An indication that lithium bromide addition is responsible for the formation of 1,2-dibromotetrafluorobenzene, came from the reaction of bromopentafluorobenzene with n-butyl-lithium in ether n-pentane solution. Lithium halides, and particularly lithium chloride, are insoluble in ether pentane and so the only nucleophile present was the pentafluorophenyl anion. The sole product detected was 2-bromononafluorobiphenyl in 56% yield.

If lithium bromide addition to the benzyne takes place, other lithium salts should add likewise. A number of such additions under "benzyne" conditions at 15° were made using various combinations of lithium halides. Pentafluorophenyl-lithium was formed in each case from bromopentafluorobenzene (2·5 g) and an excess of bromopentafluorobenzene (2·5 g). The results of these experiments are shown in Table 1.

TABLE 1

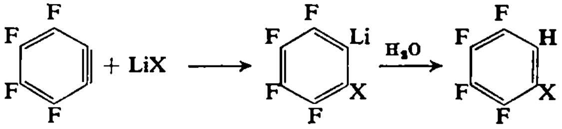
Expt.	Lithium halide Present	Total recovery (g)	C_6F_4BrH	C_6F_5I	$C_6F_4Br_2$	C_6F_4BrI	$C_6F_5C_6F_4{}^2Br$	$C_6F_5C_6{}^4F_4Br$
(b)	LiBr	2·6	—	—	2·0		0·5	0·1
(d)	LiCl	1	—	—	—	—	1·0	—
(g)	LiClLiBr	1·5	—	—	0·8	—	0·5	0·2
(e)	LiILiBr	2·3	—	0·3	0·75	0·9	0·3	—
(c)	—	2	—	—	—	—	2·0	—
(1)	LiILiCl	2·9	0·3	1·1	0·5	1·0	—	—

It can be seen that in reactions in which lithium halides have been added the proportion of 1,2-dihalogeno-tetrafluorobenzenes in the products increases markedly.

The formation of bromo compounds when lithium iodide was added can be explained either by halogen metal interchange starting from bromopentafluorobenzene or by the formation of lithium bromide in the reaction.

$$\text{n } C_4H_9Br + I^{(-)} \rightarrow \text{n } C_4H_9I + Br^{(-)}$$

which has been shown to take place under the reaction conditions used. Also the formation of 1-bromo-2,3,4,5-tetrafluorobenzene is an indication that reactions of the type represented below are proceeding.



The reaction of pentafluorobenzene with n-butyl-lithium[12] has been used to obtain further evidence for the benzyne mechanism. If metal exchange can operate when pentafluorobenzene is present in decomposing pentafluorophenyl-lithium, one of the products should be 2H-nonafluorobiphenyl. When pentafluorobenzene was added to pentafluorophenyl-lithium at −78°, a trace of 4H-nonafluorobiphenyl was the only

[12] J. Harper E. J. Soloski and C. Tamborski *J. Org. Chem.* 2385 (1964)

product isolated, but when the reaction was carried out at 15° three products were isolated. They were 1-bromo-2,3,4,5-tetrafluorobenzene identical with a sample prepared by hydrolysis of the mono-Grignard reagent from 1,2-dibromotetrafluorobenzene, 2H- and 4H-nonafluorobiphenyls, each identical with samples prepared independently. The former biphenyl was made from a crossed Ullmann reaction between bromopentafluorobenzene and 1-bromo-2,3,4,5-tetrafluorobenzene (decafluorobiphenyl and 2H,2′H-octafluorobiphenyl were also obtained) and the latter by dehydrazination of 4-hydrazinononafluorobiphenyl of known orientation.[8] These three products from the C_6F_5Li–C_6F_5H reaction fit the proposed scheme. 1-Bromo-2,3,4,5-tetrafluorobenzene comes from addition of lithium bromide to tetrafluorobenzyne followed by hydrogen metal exchange with pentafluorobenzene, the 2H-nonafluorobiphenyl comes from hydrogen metal exchange between 2-lithiononafluorobiphenyl and pentafluorobenzene, and the 4H-nonafluorobiphenyl comes from nucleophilic attack of pentafluorophenyl-lithium on pentafluorobenzene and is the expected product from such a reaction. When lithium iodide was added to the system C_6F_5Li–C_6F_5H free from other lithium halides, the sole product isolated was 1,2,3,4-tetrafluoro-5-iodo-benzene in 57% yield. The addition of lithium iodide to pentafluorophenyl-lithium gave 2-iodopentafluorobiphenyl and 1,2-diodotetrafluorobenzene. The mode of addition of lithium halide and of pentafluorophenyl-lithium to the benzyne is not clear, though stepwise ionic addition would seem more likely than the four center addition favoured by Vorozhtsov for the reaction of benzene with tetrafluorobenzyne.[5] The reaction, as postulated, does not involve the four center addition of bromopentafluorobenzene since 2H-nonafluorobiphenyl is isolated from the reaction of bromopentafluorobenzene and tetrafluorobenzyne. The 1,2-disubstituted tetrafluorobenzenes result from halogen metal interchange which has been shown can take place with 2-lithiononafluorodiphenyl. Further, lithium alkyls and aryls can add to benzyne intermediates.[13] In a previous paper[2] we suggested that the isolation of 1,2-dibromotetrafluorobenzene after bromine had been added to a reaction mixture, was evidence for direct addition of a halogen to tetrafluorobenzyne, in view of this later work we feel that it is no longer certain that this product arose by direct bromine addition; it could have come from an organo-lithium intermediate.

In the reactions we have so far described nucleophilic displacements by the pentafluorophenyl anion competed with benzyne formation. We investigated therefore the reactions of the former with other fluoro aromatic substrates. It seemed likely that at low temperatures, on reactive substrates, nucleophilic substitution would predominate. It was found that pentafluorophenyl anion is a surprisingly good nucleophile. Pentafluorophenyl-lithium reacted with perfluorobiphenyl in ether even at −40° to yield complex mixtures of polyperfluorophenyls. This reaction is similar to that of pentafluophenyl-magnesium bromide and perfluorobiphenyl in tetrahydrofuran previously reported.[14] From the mixture of polyperfluorophenyls, compounds of the type $C_6F_5(C_6F_4)_nC_6F_5 (n = 1\text{–}3)$ have been isolated. These were characterized by comparison with authentic specimens prepared by crossed Ullmann reactions[14] showing the linkage to be *para*, which is the expected orientation for nucleophilic attack on perfluorobiphenyl. Even when an excess of perfluorobiphenyl was present

[13] E. F. Jenny and J. D. Roberts, *Helv. Chim. Acta* 38, 1248 (1955).

[14] J. Thrower and M. A. White, private communication.

it was difficult to limit the chain length, indicating that the reactivity of the higher homologues towards nucleophilic attack is even greater than that of perfluorobiphenyl.

The reaction of pentafluorophenyl-lithium with octafluorotoluene afforded two major products. The first was a trifluoromethyl-nonafluorobiphenyl, the F^{19} NMR spectrum indicating that it was the 4-trifluoromethyl isomer. It was hydrolysed with fuming sulphuric acid to give a perfluorodiphenic acid which was decarboxylated to the known 4H-nonafluorobiphenyl. Thus the first product was confirmed as 4-trifluoromethylnonafluorobiphenyl (V) from the nucleophilic attacks on octafluorotoluene.[15] The second product was a trifluoromethyltridecafluoroterphenyl, F^{19} NMR spectroscopy indicating that it was a linear structure namely 4-trifluoromethyltridecafluoro-*p*-terphenyl (VI). The IR spectrum was very similar to that of perfluoro-*p*-terphenyl and very different from those of 4′,5′-bistrifluoromethylperfluoro-*o*-terphenyl and 4′ nitroperfluoro-*m*-terphenyl (see later). Again this type of orientation would be the expected one for nucleophilic attack on 4-trifluoromethyl-nonafluorobiphenyl. In several cases nucleophilic attack on biphenyl derivatives of the type $C_6F_5C_6F_4X$ (4) has given products of the type 4′-Y $C_6F_4C_6F_4$ X (4).

The reaction with perfluoro-*o*-xylene was extremely rapid and gas chromatography indicated two products which were easily separated on a preparative scale. One was a bis-trifluoromethyloctafluorobiphenyl and the other a bis-trifluoromethylperfluoroterphenyl. The structures of these components have been indicated by F^{19} NMR spectroscopy and by comparison with the results of other nucleophilic substitutions of perfluoro-*o*-xylene when chemical orientation could be carried out.[16] The first position of nucleophilic attack in these cases was in position 4 and the second in position 5. The first product therefore should be 3,4-bistrifluoromethyloctafluorobiphenyl (I) and the second 4′5′-bis-trifluoromethylperfluoro-*o*-terphenyl (II). F^{19} NMR spectroscopy supported these allocations.

Reaction between pentafluorophenyl-lithium and pentafluoronitrobenzene, which is very reactive towards nucleophilic attack[17] was carried out at −78°. Analytical gas chromatography indicated two major products with a measureable proportion of two others which could not be completely characterized. The smaller of these two components which had the shortest gas chromatographic retention time was probably a nonafluoronitrobiphenyl from IR spectroscopy and the larger and longer retained component was indicated by F^{19} NMR spectroscopy and elemental analysis to be 4-nitroperfluoro-*p*-terphenyl. The two major components were readily isolated by preparative scale gas chromatography. The first a high boiling viscous liquid was a nonafluoronitrobiphenyl. On reduction with hydrogen over Pd-C the theoretical quantity of hydrogen for one nitro group was taken up and 4-aminononafluorobiphenyl was obtained. This was identical with that prepared from 4-hydrazinononafluorobiphenyl;[8] hence the nitro compound was 4-nitrononafluorobiphenyl. This is in accord with other displacements of fluorine from pentafluoronitrobenzene by nucleophiles which cannot associate with the nitro group.[18] The second component

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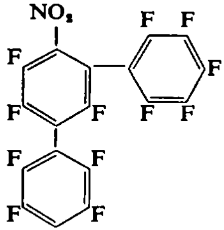
[15] D. J. Alsop, J. Burdon and J. C. Tatlow, *J. Chem. Soc.* 1801 (1962).

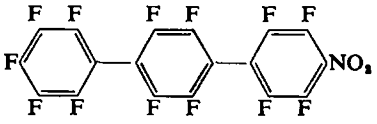
[16] E. V. Aroskar, M. T. Chaudry, R. Stephens and J. C. Tatlow, *J. Chem. Soc.* 2975 (1964).

[17] G. M. Brooke, J. Burdon and J. C. Tatlow, *J. Chem. Soc.* 802 (1961).

[18] J. G. Allen, J. Burdon and J. C. Tatlow, *J. Chem. Soc.* paper No. 4/585.

was a nitrotridecafluoroterphenyl. There were two possible structures for this compound


IX


X

based on the known orientations and ease of attack on pentafluoronitrobenzene and 4-substituted nonafluorobiphenyls. Compound X was already indicated to be one of the minor products of the reaction, and the expected F^{19} NMR spectra of the two compounds would be vastly different. It is possible using chemical shift parameters[19] to predict the approximate spectrum for each of the structures (Experimental). The spectrum predicted for IX agrees closely with the measured spectrum and we assign the structure of the terphenyl as IX namely 4′-nitroperfluoro-*m*-terphenyl.

In the reactions of pentafluorophenyl-lithium with fluoro-olefins, both decafluorocyclohexene and chlorotrifluoroethylene were attacked rapidly even at —78°.

Analysis of the products from decafluorocyclohexene revealed two components, the first having an identical gas chromatographic retention time to that of bromopentafluorobenzene with which it was obtained. This mixture was easily separated by formation and hydrolysis of Grignard reagent from bromopentafluorobenzene to give pentafluorobenzene. Separation by preparative scale gas chromatography now yielded the reaction product namely 1-pentafluorophenyl-nonafluorocyclohexene (III). This compound was identical to that prepared by the Ullmann reaction of 1-bromononafluorocyclohexene and bromopentafluorobenzene.[20]

The second product, a highly crystalline solid analysed for a bispentafluorophenyloctafluorocyclohexene. Spectroscopic examination revealed a weak stretching frequency in the IR similar to that observed in 1,2-disubstituted cyclofluoro-olefins. The UV spectrum was similar to that of *cis*-stilbene. The olefin was resistant to oxidation by both potassium permanganate in acetone and alkaline potassium permanganate. The addition of aryl-lithium reagents to cyclic fluoro-olefins[21,22] gives 1,2-disubstituted products rather than 1,1- or 1,3-systems presumably because a negative charge is more stabilized by a $-\overset{|}{\underset{|}{\mathrm{C}}}-\mathrm{Ar}$ system than by a $-\overset{|}{\underset{|}{\mathrm{C}}}-\mathrm{F}$ system. It seems probable therefore that the compound is 1,2-bispentafluorophenyloctafluorocyclohexene (IV). The reaction of pentafluorophenyl-lithium with chlorotrifluoroethylene was complex. Using molar proportions of reactants it was possible to isolate the major component, a bispentafluorophenylchlorofluoroethylene for which two structures are possible namely 1,1- and 1,2-phenyl substituents. The IR spectrum

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[19] L. F. Thomas, private communication.

[20] S. F. Campbell, R. Stephens and J. C. Tatlow, to be published.

[21] S. Dixon, *J. Org. Chem.* 21, 500 (1956).

[22] A. T. Blomquist and E. A. La Lancette, *J. Amer. Chem. Soc.* 1381 (1961).

showed a double bond stretching frequency at 1695 cm^{-1} which is similar to that of a number of 1,2-disubstituted chlorofluoroethylenes. The UV spectrum showed a *trans*-stilbene type curve. The compound was resistant to oxidation by alkaline permanganate and chromium trioxide in glacial acetic and gave pentafluorobenzoic acid in small yield. The reaction of chlorotrifluoroethylene with phenyl-lithium has been reported,[23] the major product was 1,2-bisphenylchlorofluoroethylene and was inferred as the *trans* isomer by UV spectroscopy. All the available evidence therefore suggests our compound to be 1,2-bispentafluorophenylchlorofluoroethylene (VII). By considering the stereo chemistry of the intermediates in the reaction and assuming *trans* addition and elimination the compound is the predicted one.

From the reactions described it is clear that the pentafluorophenyl anion is a versatile reagent and by careful control of the conditions a number of synthetically useful compounds can be obtained. Further work is in progress to extend the scope of these processes.

EXPERIMENTAL

Gas chromatography. Separations were carried out using a Cu-column 488 cm × 30 mm diam packed with silicone gum (Si301) on Kieselguhr 1:6. In all cases N_2 was the carrier gas.

Reactions of pentafluorophenyl lithium with bromopentafluorobenzene

(a) *Reaction at* −40°. Pentafluorophenyllithium was prepared in dry ether (30 ml)[2] from bromopentafluorobenzene (2·5 g) and n-BuLi made from n-BuBr. At −78° bromopentafluorobenzene (2·5 g) in dry ether (15 ml) was added. After being stirred at −78° for 2·5 hr, the mixture was warmed to −40° and kept at this temp for 5 days. Water (100 ml) was added, the ether layer separated and filtered to give a white solid which was washed with 4N H_2SO_4 and water to leave a residue (2·8 g). Sublimation *in vacuo* (3 × 10^{-2} mm) gave a number of fractions: which from elemental analysis and IR spectroscopy appeared to be polyphenyls of the type $C_6F_5(C_6F_4)_nC_6F_4Br$ ($n = 1$–5). For example, compound 1, sublimed at 190° and 0·3 mm was analysed. (Found. C, 42·7; Br 10·2. $C_{24}F_{17}Br$ requires: C, 41·7; Br, 11·5%.) Compound 2, sublimed at 250° and 0·05 mm was analysed. (Found: C, 43·5, Br. 8·9. $C_{30}F_{21}Br$ requires: C, 42·9; Br, 9·5%.) The ether solution was dried ($MgSO_4$) and distilled to give a semisolid residue, which on gas chromatographic separation (150° 15 lN_2/hr) gave (1) 1,2-dibromotetrafluorobenzene (0·1 g) identical with an authentic specimen; (ii) 2-bromo nonafluorodiphenyl (0·1 g) m.p. 67–68° and (iii) 4-nonafluorobiphenyl (0·8 g) m.p. 97·98°. The last two products were identical with specimens prepared by independent synthesis (see below).

(b) *Reaction at* 15°. Pentafluorophenyl-lithium prepared as in (a) from bromopentafluorobenzene (2·5 g) in dry ether was stirred at −78° for 15 min. The mixture was rapidly warmed to 15° and bromopentafluorobenzene (2·5 g) added. After being stirred at 15° for 18 hr, the mixture was centrifuged to remove precipitated salts (0·08 g) mainly LiF. The ether layer was washed 4N H_2SO_4 (100 ml) dried ($MgSO_4$) and distilled. The residue which was separated by gas chromatography (150° 15l/N_2/hr) gave (i) 1,2-dibromotetrafluorobenzene (2·0 g); (ii) 2-bromo-nonafluorobiphenyl (0·5 g); (iii) 4-bromo-nonafluorobiphenyl (0·1 g), identical with authentic specimens and a trace of a compound with the same GPC retention time and similar IR spectrum to 2H-nonafluorobiphenyl (see below).

(c) *Reaction in ether pentane at* 15°. Bromopentafluorobenzene (5·0 g) in dry ether (30 ml) was added to n-BuLi (0·64 g) prepared from n-BuCl in n-pentane (8 ml). After being stirred at 15° for 18 hr, the mixture was washed with 4N H_2SO_4 (100 ml), the ether solution dried ($MgSO_4$) and the solvents removed to give as the sole product 2-bromo-nonafluorobiphenyl (2 g) m.p. 67–68° identical with an authentic specimen.

(d) *Reaction in the presence of excess* LiCl. Bromopentafluorobenzene (2·5 g) and n-BuLi from n-BuCl in dry ether (20 ml) were stirred at −78° for 15 min. Bromopentafluorobenzene (2·5 g) in dry ether (10 ml) was added, the mixture warmed to 15° and stirred for 4 hr. After being washed

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[23] R. Meier and F. Böhler, *Chem. Ber.* **90**, 2344 (1957).

with water (100 ml) and 4N H_2SO_4 (100 ml) the ether layer was dried ($MgSO_4$) and distilled. The semi-solid residue was separated by gas chromatography (150° 14lN_2/hr) to give (i) a liquid (0·02 g) the IR spectrum of which indicated 1-bromo-2-chloro-tetrafluorobenzene; (ii) 2-bromo-nonafluorobiphenyl (1·0 g) and (iii) 4-bromo-nonafluorobiphenyl (trace) all identical with authentic specimens.

(e) *Reaction in the presence of* LiBr *and excess* LiI. To pentafluorophenyl-lithium at −78° (from C_6BrF_5, 2·5 g and BuLi from n-BuBr) was added LiI (10 g) in dry ether (15 ml). The mixture was warmed to 15° and bromopentafluorobenzene (2·5 g) was added. After being stirred for 3·5 hr, the mixture was washed with water (100 ml) dried ($MgSO_4$) and distilled. Gas chromatographic separation of the residue (150° 14lN_2/hr) gave (i) iodopentafluorobenzene (0·3 g); (ii) 1,2-dibromotetrafluorobenzene (0·75 g); (iii) *1-bromo 2-iodotetrafluorobenzene* (0·9 g) b.p. 260–262°, (Found: C, 21·0; I, 35·6; C_6F_4BrI requires: C, 20·2 I, 35·8%) and (IV) 2-bromononafluorobiphenyl (0·3 g). The known products were identified by comparison with authentic specimens.

(f) *Reaction in the presence of* LiCl *and excess* LiI. From an experiment similar to (e) but using n-BuLi prepared from n-BuCl there was obtained (i) 1-bromo-2,3,4,5-tetrafluorobenzene (0·3 g); (ii) iodopentafluorobenzene (1·1 g); (iii) 1,2-dibromotetrafluorobenzene (0·5 g) and (iv) 1-bromo-2-iodo-tetrafluorobenzene (1·0 g) b.p. 260–261 all identical with authentic specimens.

(g) *Reaction in the presence of* LiBr *and excess* LiCl. Pentafluorophenyl-lithium (from C_6BrF_5, 2·5 g and BuLi from BuBr) was stirred at −78° for 15 min, when LiCl (10 g) and bromopentafluorobenzene (2·5 g) was added. The mixture was rapidly warmed to 15° and stirred for 2 hr. Working up followed by gas chromatographic separation afforded (i) 1,2-di-bromotetrafluorobenzene (0·8 g); (ii) 2-bromononafluorobiphenyl (0·5 g) and (iii) 4-bromo-nonafluorobiphenyl (0·2 g) all identical with authentic specimens.

Reaction of pentafluorophenyl lithium in the presence of LiI

Pentafluorophenyl-lithium (from C_6F_5I, 5 g and n-BuLi from n-BuCl) in 3:1 ether n-heptane (15ml) and LiI (1·4 g) were stirred at −78° for 15 min. The mixture was warmed to 15° and stirred 3·5 hr. Working up and gas chromatographic separation (178° 15lN_2/hr) gave (i) pentafluoroiodobenzene (1·0 g); (ii) 1,2-di-iodotetrafluorobenzene (1·5 g) and (iii) 2-iodononafluorobiphenyl (0·2 g), all identical with authentic specimens.

Reaction of 2-lithiononafluorobiphenyl with iodo-pentafluorobenzene

n-Butyl-lithium (0·33 g) in 3:1 ether–heptane (10 ml) was added to a stirred solution of 2-bromononafluorobiphenyl (1·7 g) in dry ether (10 ml) at −78°. After being stirred at −78° for 15 min, the mixture was worked up and gas chromatography separation (176° 15lN_2/hr) gave (i) 2,H-nonafluorobiphenyl (0·1 g) and (ii) 2-iodononafluorobiphenyl (1·2 g) m.p. 32–33° (lit. 34–35[4]) with IR spectrum identical to that of authentic samples.[4]

Reaction of pentafluorophenyl-lithium with pentafluorobenzene

(a) *At* −78°. To pentafluorophenyl-lithium (from C_6BrF_5, 2·5 g and BuLi from BuBr) at −78° was added pentafluorobenzene (1·7 g). After being kept at −78° for 2 hr, the mixture was warmed to and maintained at −40° for 2 days. Working up, followed by gas chromatographic separation (130° 15lN_2/hr) afforded pentafluorobenzene (2·1 g) and a trace of 4H-nonafluorobiphenyl.

(b) *At* 15°. Pentafluorophenyl-lithium (from C_6F_5H, 1·7 g and BuLi from BuBr[12]) was stirred at −78° for 15 min. To the stirred solution pentafluorobenzene (1·7 g) was added and the mixture rapidly warmed to 15° and stirred at 15° for 3 hr. After work up, gas chromatographic separation gave (i) 1,bromo-2,3,4,5-tetrafluorobenzene (1·9 g); (ii) 2-H-nonafluorobiphenyl (0·35 g) and (iii) 4H-nonafluorobiphenyl (0·1 g), all identical with authentic specimens (see below).

(c) *Reaction in the presence of* LiI. Anhydrous LiI (1·5 g) in dry ether (20 ml) was added to an ethereal solution of pentafluorophenyl-lithium (from C_6F_5H, 1·7 g and n-BuLi from n-BuCl) at −78°. While the temp rose to 15°, pentafluorobenzene (1·7 g) in ether (10 ml) was added. After being kept for 5 hr at 15°, the mixture was worked up to give after gas chromatographic separation (160° 15lN_2/hr) (i) pentafluorobenzene (0·8 g) and (ii) 1,2,3,4-tetrafluoro-5-iodobenzene (1·6 g) b.p. 159–160°. (Found: C, 26·9; H, 0·4. C_6HF_4I requires: C, 26·1; H, 0·4%.)

2, *H-nonafluorobiphenyl.* Bromopentafluorobenzene (2·5 g), 1-bromo-2,3,4,5-tetrafluorobenzene (2·3 g) and Cu-bronze (4·0 g) were heated together in a sealed tube at 210° for 17 hr. Extraction of the products with ether (50 ml) followed by gas chromatographic separation (150° 15 *l*N_2/hr) gave (i) perfluorobiphenyl (0·6 g); (ii) 2H-nonafluorobiphenyl m.p. 42–43° (Found: C, 45·2; H:0·5 $C_{12}F_9H$ requires: C, 45·5; H, 0·32%) and (iii) 2H2'H-octafluorobiphenyl (0·2 g) m.p. 73–78°. (Found C, 48·0; H, 0·8 $C_{12}H_2F_8$ requires C, 48·3; H, 0·7%.)

2-Bromononafluorobiphenyl. Bromopentafluorobenzene (2·5 g), 1,2-dibromotetrafluorobenzene (3·1 g) and Cu-bronze (5 g) were heated together in a sealed tube at 210° for 16 hr.

The products were extracted with ether (100 ml), the ether evaporated and the residue separated by gas chromatography (180° 15 *l*N_2/hr) to give (i) perfluorobiphenyl (0·01 g); (ii) 2-bromononafluorobiphenyl (0·5 g) m.p. 67–68° cited 69° (Found; C, 36·7; Br, 21·0 $C_{12}F_9Br$ requires; C, 36·5; Br. 20·3%) and (iii) 2,2'-dibromooctafluorobiphenyl (1·2 g) m.p. 98–99° (Found: C, 31·5; H, 0·0. $C_{12}Br_2F_8$ requires; C, 31·6; H, 0·0%).

4-Bromononafluorobiphenyl. To 4-hydrazinononafluorobiphenyl (3·5 g)[8] in glacial acetic acid (40 ml) was added Br_2 (3·2 g) in glacial acetic acid (12 ml). The mixture was stirred at 15° for 1½ hr, refluxed 22 hr and then poured into water (200 ml). The precipitate was dissolved in ether and the ether layer washed with sodium metabisulphite solution and water. After it had been dried ($MgSO_4$) the ether was evaporated to leave a crystalline solid (2 g). Sublimation *in vacuo* and recrystallization from EtOH gave 4-bromononafluorobiphenyl (1·8 g) m.p. 102–103°, (Found: C, 37·1; Br, 20·2. $C_{12}F_9Br$ requires: C, 36·5; Br, 20·2%.)

Reaction of pentafluorophenyl-lithium with perfluorobiphenyl

Perfluorobiphenyl (4·0 g) in ether (10 ml) was added with stirring at −78° to pentafluorophenyl-lithium (from C_6BrF_5, 2·5 g and n-BuLi from BuBr). After 1 hr, the reaction mixture was warmed to −40° and kept at this temp for 5 days, and then water (100 ml) was added. The precipitated solid (0·7 g) was removed, the ether layer washed with water and dried ($MgSO_4$) and evaporated to leave a solid mass (1·3 g) which was shown by analytical gas chromatography to be a complex mixture of products. Fractional sublimation of both ether soluble and insoluble fractions gave respectively:

(a) (*ether soluble*) (i) Perfluorobiphenyl (0·7 g) m.p. 67–68° (sublimation 85°/10 mm); (ii) a mixture of perfluorobi- and terphenyls 0·1 g (150°/10 mm); (iii) perfluoro-*p*-terphenyl (0·2 g) m.p. 176–178° (170/10 mm) and (iv) perfluoro-*p*- quaterphenyl (0·1 g) m.p. 224–226° (155/05 mm).

(b) *ether insoluble.* (i) perfluorobiphenyl (0·01 g) m.p. 67–68° (60/·01 mm); (ii) perfluoro-*p*-terphenyl (0·07 g) m.p. 188° (110°/01 mm), (iii) perfluoro-*p*-quaterphenyl (0·4 g) m.p. 222 (160°/05 mm) and (iv) perfluoro-*p*-quinquephenyl (0·1 g) m.p. 288–290° (240°/05 mm) + higher unsublimable perfluoropolyphenyls.

These compounds were identified by comparison of their IR spectra and m.ps with those of authentic specimens prepared by crossed Ullmann reactions.[14]

Reaction with perfluorotoluene

Perfluorotoluene (0·95 g) was added with stirring to ethereal pentafluorophenyl-lithium (from C_6BrF_5, 1 g and BuLi from BuBr.) After being stirred for 1 hr at −78°, the reaction mixture was kept at −40° for 10 days and then water (100 ml) was added. The ether layer and the ethereal extracts of the aqueous layer were combined, dried ($MgSO_4$) and evaporated to give a low melting solid (1·0 g) which on gas chromatographic separation (180° 14*l*N_2/hr) gave (i) 4-trifluoromethylnonafluorobiphenyl (0·5 g) m.p. 32–33° from EtOH (Found: C, 40·8; H, 0·0, $C_{13}F_{12}$ requires: C, 40·6; H, 0·0%) and (ii) 4-trifluoromethyltridecafluoro-*p*-terphenyl (0·2 g) m.p. 151–152° from EtOH. (Found: C, 42·8; F, 56·5. $C_{18}F_{16}$ requires: C, 42·9; F, 57·1%.)

Hydrolysis of 4-trifluoromethylnonafluorobiphenyl

The biphenyl (0·5 g) was heated with fuming H_2SO_4 (1 ml) in a sealed tube at 160° for 15 hr. The product was poured onto ice and extracted continuously with ether for 15 hr. The ether layer was washed with Na_2CO_3 aq and the carbonate layer acidified and extracted continuously with ether for 15 hr. The ether layer was dried ($MgSO_4$) and evaporated to leave *4-carboxynonafluorobiphenyl* (0·4 g) m.p. 175–176° from petrol 100–120°. (Found: C, 43·1; H, 0·4; equiv. wt. 363. $C_{13}HF_9O_2$ requires; C, 43·3; H, 0·3% equiv. wt. 360.) A sample of the acid was heated with soda-lime *in vacuo* to give 4H-nonafluorobiphenyl[8] m.p. and mixed m.p. 77°, with an IR spectrum identical to that of an authentic specimen.

Reaction with perfluoro-o-xylene

Perfluoro-*o*-xylene (2·9 g) in dry ether (10 ml) was added with stirring to a solution of pentafluorophenyl-lithium (from C_6BrF_5, 2·5 g and BuLi from BuBr) in ether at −78°. After 15 min, the mixture was warmed to 16° and kept for 18 hr. The ether layer was washed with 4N H_2SO_4 (100 ml) and dried ($MgSO_4$). Evaporation of the solvent gave a semisolid which gave on gas chromotographic separation (160° 15/N_2/hr) (i) 3,4-bistrifluoromethyloctafluorobiphenyl (1·0 g) m.p. 43–45° (Found: C, 38·1; $C_{14}F_{14}$ requires: C, 38·79.) and (ii) 4′,5′-bistrifluoromethylperfluoro-*o*-terphenyl (0·4 g) m.p. 101–102°. (Found: C, 41·3; F, 59·3. $C_{20}F_{18}$ requires: C, 41·2; F, 58·7%.)

Reaction with pentafluoronitrobenzene

Pentafluoronitrobenzene (1 g) in dry ether (10 ml) was added with stirring to an ethereal solution of pentafluorophenyl-lithium (from C_6BrF_5, 2·5 g and BuLi from BuBr) at −78°. After being kept at −78° for 1 hr, the mixture was warmed to 15° and then allowed to stand for 18 hr. The ether layer was washed 4N H_2SO_4 (100 ml) and water (100 ml) and dried ($MgSO_4$). Evaporation of the ether and gas chromatographic separation of the residue gave (i) 4-nitrononafluorobiphenyl (0·6 g) b.p. 257–259° (Found: C, 40·1; H, 0·0 $C_{12}F_9NO_2$. requires: C, 39·9; H, 0%) and (ii) 4′-nitroperfluoro-*m*-terphenyl (0·8 g) m.p. 108–109°. (Found: C, 42·1; H, 0·0; mol. wt. 506. $C_{18}F_{13}NO_2$ requires: C; 42·4; H, 0·0% mol. wt. 509.)

Characterization of 4-nitrononafluorobiphenyl

(a) The nitro compound (0·3 g) in EtOH (5 ml) was hydrogentated at atm. press. using Pd-C as catalyst. Evaporation of the solvent afforded 4-aminononafluorobiphenyl (0·2 g) m.p. 142–143°.

(b) 4-Hydrazinononafluorobiphenyl (2·6 g) and 54% HI (5 ml) were refluxed for 4 hr. After removal of I_2 with sodium metabisulphite, the reaction mixture was distilled in steam to give 4-aminononafluorobiphenyl (2 g). Sublimation at 115°/10 mm gave a pure product m.p. and mixed m.p. with the product from (a) 142–143°. (Found: C, 43·3; H, 1·0, $C_{12}H_2F_9N$ requires: C, 43·5; H, 0·6%.)

Reaction with decafluorocyclohexene

To an ethereal solution of pentafluorophenyl-lithium (from C_6BrF_5, 5 g and BuLi from BuBr) at −78° was added decafluorocyclohexene (5·3 g) in dry ether (15 ml). After being stirred at −78° for 2 hr, the mixture was warmed to 15° and kept for 18 hr. The precipitated solid, mainly LiF, was centrifuged off, the ether layer washed with 4N H_2SO_4 (100 ml) and water (50 ml) and dried ($MgSO_4$). Evaporation of the ether and separation by gas chromatography (150° 15/N_2/hr) gave (i) a mixture of bromopentafluorobenzene and 1-pentafluorophenylnonafluorocyclohexene (1·75 g) and (ii) 1,2-bispentafluorophenyloctafluorocyclohexene (0·9 g) m.p. 138–139°. (Found: C, 39·4; F, 61·3. $C_{18}F_{18}$ requires: C, 38·9; F, 61·4%) max. 248·0 Å (ε 3180) in EtOH.

Separation of (i). The mixture (1·75 g) was stirred and refluxed 3 hr with Mg turnings (0·5 g) in dry ether (10 ml). Water (50 ml) was added, the ether layer dried ($MgSO_4$) and separated by gas chromatography (120° 15/N_2/hr) to gave 1-pentafluorophenylnonafluorocyclohexene (1·0 g) b.p. 174–175° identical with a specimen prepared by an Ullmann reaction between 1-bromo-nonafluorocyclohexene and bromopentafluorobenzene.[30]

Reaction with chlorotrifluoroethylene

Chlorotrifluoroethylene (2·4 g) was added to ethereal pentafluorophenyl-lithium (from C_6BrF_5, 5 g and BuLi from BuBr) at −78°. After being stirred at −78° for 2 hr, the mixture was warmed to 15° and kept 18 hr. A precipitate (1·3 g) formed and was filtered off and the ether layer worked up to yield a solid residue (0·4 g). The solids were recrystallized from EtOH to give 1,2-bispentafluorophenyl-1-fluoro-2-chloroethylene m.p. 118–120°. (Found: C, 41·0, $C_{14}F_{11}Cl$ requires: C, 40·7%.) λ_{max} 2550 Å (ε 18,800) in EtOH.

F^{19} *Nuclear magnetic resonance*

The spectra were recorded on a Varian HR 100 spectrometer at 94·1 Mc/s with trifluoroacetic acid as internal reference. Chemical shifts were calculated relative to hexafluorobenzene at 88 ppm relative to trifluoroacetic acid.

1. *4-Nitrononafluorobiphenyl.* The spectrum showed five groups of chemically shifted peaks as shown in Table 2.

Using the F^{19} shift parameters for nitro and pentafluorophenyl substituents in fluoro-aromatic rings and assuming these effects are additive it is possible to predict the spectra of the various isomers of nitrononafluorobiphenyl. The F^{19} shift parameters for—NO_2 C_6F_5 and CF_3 are shown in Table 3

TABLE 2

Peak	TFA Shift c/s	C_6F_6 ppm	Rel. intensity
1	5100	−33·6	2
2	5350	−31	2
3	6150	−23	2
4	6350	−20	1
5	7400	−9	2

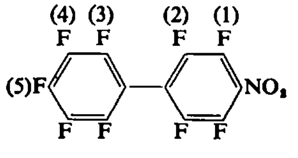
TABLE 3

Position relative to substituent		Substituents	
	NO_2	C_6F_5	CF_3
ortho	−17 ppm	−24	−24·9
meta	−4	−1·5	−2
para	−16	−12	−14·8

TABLE 4

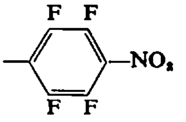
Ring position	Shift rel. to C_6F_6	Assignment line
1	−18·5	3
2	−28	1
3	−24	2
4	−1·5	5
5	−12	4

Using these parameters the predicted shifts for the ring fluorine atoms in



are shown in Table 4.

Although not corresponding exactly to the observed spectrum the predicted spectrum shows the correct trend and spacings between peaks. Further the predicted spectra of the *ortho* isomers are greatly different from the 4-substituted compound. We can now use the shifts caused by the



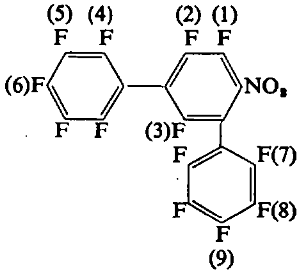
group to predict the spectrum of other compounds.

(2) *4′-Nitroperfluoro-*m*-terphenyl.* The spectrum showed seven groups of chemically shifted peaks as shown below in Table 5

TABLE 5

Peak	Shifts TFA (c/s)	C_6F_6(ppm)	Rel. intensity
1	2750	−59	1
2	4100	−49	1
3	5300	−32	2
4	5430	−30	2
5	6050	−24	1
6	6350	−20	2
7	7400	−9	4

Using the parameters previously described the predicted shifts for



F. atom	Calc. shift	Peak
1	−20	5
2	−40	2
3	−52	1
4	−31	3 or 4
5	−9	7
6	−20	6
7	−31	3 or 4
8	−9	7
9	−20	6

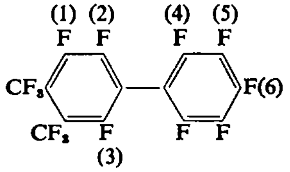
These shifts reasonably agree with those observed and taking the multiplicity of each peak into account the assignments shown can be made. The predicted spectra of the other isomers are considerably different from that observed and would appear to eliminate these structures for the compound.

(3) *4-Bistrifluoromethylperfluorobiphenyl.* The spectrum shows six chemically shifted groups of peaks other than that for the trifluoromethyl group and are shown in Table 6.

TABLE 6

Peak	Shift TFA (c/s)	C_6F_6 ppm	Rel. intensity
1	2600	−60	1
2	3750	−48	1
3	5000	−36	1
4	5200	−33	2
5	6200	−22	1
6	7200	−11	2

Using the parameters given above for



the predicted spectrum is shown below:

F. atom	Calc shift	Assignment peak
1	−28	3
2	−41	2
3	−50	1
4	−24	4
5	−2	6
6	−12	5

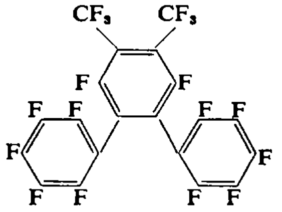
Calculation of the shifts for the other isomers show considerable differences to the observed spectrum whilst the calculated shifts given above are in reasonable agreement with the spectrum observed.

4. *4′5′-Bistrifluoromethylperfluoro-o-terphenyl.* The spectrum shows four groups of chemically shifted peaks other than those due to the trifluoromethyl group as shown below in Table 7.

TABLE 7

Peak	Shifts TFA c/s	C_6F_6 ppm	Rel. intensity
1	2900	57	1
2	5000	28	2
3	6400	20	1
4	7500	8	2

Using the parameters above for



F. atom	Calc. shift	Assignment peak
1	51	1
2	29	2
3	12	4
4	2	3

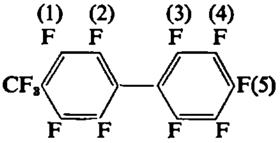
The calculated shifts are in reasonable agreement with the observed spectra and together with the observed multiplicities indicate the structure of the compound to be correctly assigned.

5. *4-Trifluoromethylnonafluorobiphenyl.* The spectrum showed five groups of chemically shifted peaks other than that for the trifluoromethyl group, which was a clear triplet indicating it to be flanked by two fluorine atoms thus eliminating substitution *ortho* to the C_6F_5 group. The remaining peak positions are shown below in Table 8.

TABLE 8

Peak	Shift TFA c/s	C_6F_6	Rel. intensity
1	3720	−28·6	2
2	3900	−25·5	2
3	4020	−23·4	2
4	4500	−14·9	1
5	5160	−3·5	2

The calculated shifts for



are shown below

F. atom	Calc. shift	Assignment peak
1	26	3
2	26	2
3	24	1
4	2	5
5	12	4

The calculated shifts are in reasonable agreement with those observed and indicate the structural assignment is correct.

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