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PERFLUOROPHENYL DERIVATIVES OF THE ELEMENTS
X*. THE FORMATION OF POLYHALOBIPHENYL DERIVATIVES FROM TRIFLUOROBROMOBENZYNE, AND SOME RELATED REACTIONS[1]

S. C. COHEN, D. E. FENTON, D. SHAW AND A. G. MASSEY
Department of Chemistry, Queen Mary College, London, E. 1. (Great Britain)

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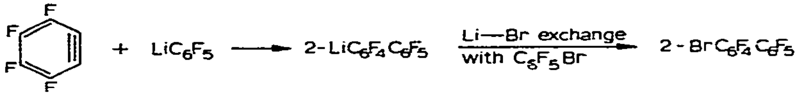
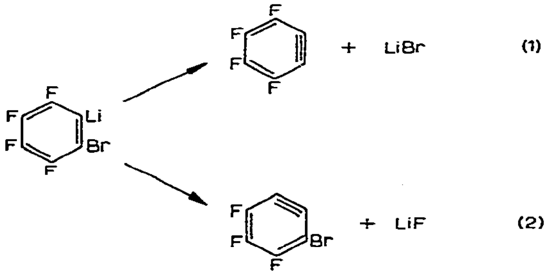
Previously, pentafluorophenyllithium has been shown to be thermally unstable towards the loss of lithium fluoride, generating what appears to be tetrafluorobenzyne[2] in solution. A second molecule of pentafluorophenyllithium can add across the triple bond of the tetrafluorobenzyne to give 2-lithiononafluorobiphenyl:



This addition is a relatively clean reaction and, if carried out in the presence of an excess of bromopentafluorobenzene, about a 30% yield of pure 2-bromononafluorobiphenyl can be isolated from the products[3-5]. We therefore considered that a study of the thermal decomposition of 1-lithio-2-bromotetrafluorobenzene was of interest to ascertain whether benzyne formation occurred by loss of either lithium fluoride or lithium bromide:



and if route (2) were favoured, could polyhalobiphenyls be obtained in useful quantities.

EXPERIMENTAL

The reactions were carried out under an atmosphere of dry, oxygen-free nitrogen; analyses were performed by Dr. A. Bernhardt of the Max-Planck-Institute, Mülheim, Germany. The molecular weights were determined by Miss B. Harman of this laboratory using a Mechrolab vapour phase osmometer, model 301A. The

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* For Part IX, see ref. 1.

fluoro-aromatic starting materials were kindly donated by the Imperial Smelting Corporation.

Preparation of (2-bromotetrafluorophenyl) lithium

1,2-Dibromotetrafluorobenzene was placed in a 3-necked flask cooled to −78° and an equimolar quantity of butyllithium added; after 15 min water was added and the mixture warmed to room temperature. On removal and drying of the ether layer, 1-hydro-2-bromotetrafluorobenzene was found to be the major component and was purified by large scale vapour phase chromatography (Perkin–Elmer Fractometer, model 451 using silicone grease column and nitrogen carrier gas). (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%.)

Reaction of 1,2-dibromotetrafluorobenzene with (2-bromotetrafluorophenyl) lithium

Butyllithium (9 ml of a 16% hexane solution) was added to a stirred solution of 1,2-dibromotetrafluorobenzene (5.4 g) in 40 ml of ether at −78°. The mixture was stirred for 3 h at −78° and, after a further 5.4 g of 1,2-dibromotetrafluorobenzene had been added, the mixture was warmed to room temperature and allowed to stand for 14 h. The ether layer was separated and volatile components (ether, butyl bromide, hexane and excess 1,2-dibromotetrafluorobenzene) removed by vacuum distillation before the solid products were sublimed at 100° in a good vacuum; the resulting white solid mixture was then separated into its components by vapour phase chromatography. Several products were observed to be present but all except two occurred to only a minor extent; these two were tribromoheptafluorobiphenyl isomers and occurred in essentially equal amounts:

2,6,2'-Tribromoheptafluorobiphenyl. M.p. 112–113°. (Found: C, 27.8; H, 0.0; Br, 46.5; F, 25.5; mol. wt., 496. $C_{12}Br_3F_7$ calcd.: C, 27.9; H, 0.0; Br, 46.4; F, 25.7%; mol. wt., 508.) The molecular formula was verified by the mass spectrum (A.E.I., MS9 instrument) and the principal fragmentation peaks were those formed by stepwise loss of bromine. The position of bromine-substitution was deduced from the ^{19}F nuclear magnetic resonance (NMR) spectrum of the sample run as a saturated solution in carbon tetrachloride, see Discussion.

2,3,2'-Tribromoheptafluorobiphenyl. M.p. 92–93°. (Found: C, 27.7; H, 0.0; Br, 46.7; F, 25.4; mol. wt., 515. $C_{12}Br_3F_7$ calcd.: C, 27.9; H, 0.0; Br, 46.4; F, 25.7%; mol. wt., 508.) The molecular formula was again verified by taking the mass spectrum, and the position of bromine-substitution deduced from the ^{19}F NMR spectrum of a sample run as a saturated solution in carbon tetrachloride, see Discussion.

Other products. Those were identified by comparison of VPC retention times and infrared spectra to authentic samples made as described later in the experimental section:

(1) 2,2'-dibromooctafluorobiphenyl[5], m.p. 97.5–98.5°.
(2) 4-bromononafluorobiphenyl[5], m.p. 97–99°.
(3) 2-bromo-2'-hydrooctafluorobiphenyl, liquid at room temperature.
(4) 2-bromononafluorobiphenyl, m.p. 69–71°.
(5) 2-hydrononafluorobiphenyl, m.p. 41–42°.

Mass spectral evidence was also obtained for trace quantities of $C_{18}F_{10}Br_4$, $C_{18}F_{11}Br_3$, $C_{12}F_6Br_4$ and another isomer(s) of $C_{12}F_8Br_2$ but the yields were much too small to enable structural investigations to be carried out. No change in the products or in their relative concentrations could be detected on carrying out the reaction, including the addition of butyllithium, wholly at room temperature.

Exchange reaction between pentafluorophenyllithium and 1,2-*dibromotetrafluorobenzene*

At −78°. An equimolar mixture of pentafluorophenyllithium and 1,2-dibromotetrafluorobenzene after being held at −78° for 2 h was hydrolysed with distilled water; pentafluorobenzene was the only aromatic compound containing hydrogen to be found in the products indicating little or no lithium–bromine exchange had occurred at this temperature.

At room temperature. A similar experiment conducted at room temperature for one hour showed that the hydrolysis products were pentafluorobenzene and 1-bromo-2-hydrotetrafluorobenzene, indicating lithium–bromine exchange had occurred.

Decomposition of pentafluorophenyllithium in the presence of 1,2-*dibromotetrafluorobenzene*

Pentafluorophenyllithium (prepared from equimolar quantities of butyllithium in hexane and bromopentafluorobenzene) was prepared at −78° and an equimolar amount of 1,2-dibromotetrafluorobenzene added before the mixture was allowed to warm up to room temperature, after stirring the solution overnight the ether was removed and the remaining viscous liquid analysed by vapour phase chromatography. Several major components, and some minor ones, were identified, either by trapping out samples for analysis or by comparison to authentic samples.

1,2-*Dibromotetrafluorobenzene.* Mainly unchanged starting material. When the pentafluorophenyllithium was prepared from iodopentafluorobenzene 1-iodo-2-bromotetrafluorobenzene was also isolated as a minor product.

2-*Bromononafluorobiphenyl*, M.p. 69–71°. (Found: C, 36.6; H, 0.1; F, 43.3; Br, 20.1. $C_{12}BrF_9$ calcd.: C, 36.5; H, 0.0; F, 43.3; Br, 20.2%.)

2,2′-*Dibromooctafluorobiphenyl.* Identity checked by comparison to an authentic specimen and the molecular formula verified by mass spectral analysis.

2,6-*Dibromooctafluorobiphenyl.* Identity checked by mass spectrometry and supported by ^{19}F NMR spectroscopy.

Among the minor components identified were pentafluorobenzene, 1-bromo-2-hydrotetrafluorobenzene and 2-hydrononafluorobiphenyl.

Preparation of 2,2′-*dibromooctafluorobiphenyl*

n-Butyllithium (40 ml, 16% solution in hexane; 0.0625 moles) was added to a solution of 1,2-dibromotetrafluorobenzene (19.25 g, 0.0625 moles) in diethyl ether (250 ml) at −78° and the mixture stirred for 15 min. Excess titanium tetrachloride (10 ml) was added and stirring continued for a further 4 h at −78° before the temperature was allowed to rise slowly up to about 20° and the mixture left overnight. Water (250 ml) was then added during stirring (1 h) and the yellow-orange organic layer separated from the violet aqueous solution [shown to contain $Ti(H_2O)_6^{3+}$], dried over magnesium sulphate, filtered and the cosolvents removed under vacuum. Yield of 2,2'-dibromooctafluorobiphenyl, m.p. 97.5–98.5°, 12.5 g or 88%. (Found: C, 31.8; H, 0.05; Br, 35.3; F, 33.1; mol.wt., 458. $C_{12}Br_2F_8$ calcd.: C, 31.6; H, 0.0; Br, 35.1; F, 33.3%; mol.wt., 456.) In this type of coupling reaction only the one product is obtained.

Preparation of 4-bromononafluorobiphenyl

n-Butyllithium (16 ml) was added at −78° to a stirred solution of bromopentafluorobenzene (6.2 g) in 40 ml of diethyl ether. After 30 min, 1,4-dibromotetrafluorobenzene (7.7 g in 50 ml of ether) was added, to be followed 15 min later by an additional 16 ml of butyllithium solution. Titanium tetrachloride (6 ml) was then added and the orange-yellow mixture stirred at −78° for 1½ h before the temperature was allowed to rise to 20° when stirring was continued for a further 21 h. After hydrolysis, separation and drying of the organic layer the solvent was removed under vacuum and the solid products separated by large-scale vapour phase chromatography. The first and third components to be eluted were decafluorobiphenyl and 4,4'-dibromooctafluorobiphenyl respectively; the second component was 4-bromononafluorobiphenyl, m.p. 97–99°, *ca.* 20% yield. (Found: C, 36.8; H, 0.1; Br, 20.2; F, 43.3. $C_{12}BrF_9$ calcd.: C, 36.5; H, 0.0; Br, 20.2; F, 43.3%.)

Preparation of 2-bromo-2'-hydrooctafluorobiphenyl

n-Butyllithium (6.5 ml, 0.01 mole) was added to a solution of 2,2'-dibromooctafluorobiphenyl (4.56 g, 0.01 mole) in 75 ml of ether at −78° and the mixture stirred for 2 h before 40 ml of water was added, temperature then being allowed to rise to 20° for 2 h. The organic layer was separated, dried with magnesium sulphate and the solvent removed under vacuum; on large-scale vapour phase chromatography the reaction product was resolved into three components, the first and third being 2,2'-dihydrooctafluorobiphenyl and 2,2'-dibromooctafluorobiphenyl respectively. The second, and major, component was the liquid 2-bromo-2-hydrooctafluorobiphenyl. (Found: C, 38.3; H, 0.1; Br, 20.9; F, 40.4. $C_{12}HBrF_8$ calcd.: C, 38.2; H, 0.3; Br, 21.2; F, 40.3%.)

Infrared spectra

2,6,2'-C_6F_4Br–$C_6F_3Br_2$ (as a mull in nujol and hexachlorobutadiene): 1628 w, 1605 m, 1548 m, 1513 ssh, 1490 s, 1474 s, 1414 s, 1389 w, 1307 w, 1275 w, 1259 w, 1227 vw, 1128 s, 1077 ssh, 1020 w, 1002 w, 990 s, 893 s, 826 s, 770 m, 757 w, 730 s, 714 s, 712 s, 695 m.

2,3,2'-C_6F_4Br–$C_6F_3Br_2$ (as above): 1628 w, 1610 m, 1587 w, 1511 s, 1471 s, 1447 s, 1412 w, 1374 m, 1250 m, 1136 m, 1093 s, 1075 sh, 1052 msh, 1049 s, 990 s, 869 m, 827 s, 805 s, 770 w, 751 w, 729 bd, 706 w, 659 m.

4-$BrC_{12}F_9$ (as above): 1661 w, 1639 w, 1531 s, 1504 s, 1484 s doublet, 1261 m, 1125 m, 1116 m, 1030 w, 998 s, 966 s, 841 w, 723 s.

2-H-2'-Br-$C_{12}F_8$ (liquid film): 1623 m, 1605 m, 1531 s, 1506 ssh, 1497 s, 1488 ssh, 1466 s, 1412 m, 1383 w, 1355 w, 1321 m, 1272 w, 1200 m, 1136 w, 1100 s, 1098 ssh, 1066 s, 1060 ssh, 1012 s, 935 m, 867 m, 829 s, 767 w, 750 w, 739 s, 698 m, 687 m.

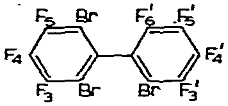
DISCUSSION

The reaction between 1-lithio-2-bromotetrafluorobenzene and 1,2-dibromotetrafluorobenzene carried out in an ether/hexane solvent is a complex one and vapour phase chromatography, using a silicone column and helium as the carrier gas, shows that up to 26 components may be present in the final reaction mixture; many, however, are present in only trace amounts. The components eluted first were shown to be solvents (ether, hexane and slight impurities in these), unchanged 1,2-dibromotetrafluorobenzene, and 1-hydro-2-bromotetrafluorobenzene, the latter probably being formed by adventitious hydrolysis of undecomposed 1-lithio-2-bromotetrafluorobenzene during work-up of the reaction mixture. The small amount of 2-bromononafluorobiphenyl detected among the products was traced back to the presence of about 1% impurity of bromopentafluorobenzene in the starting material:

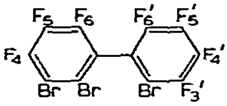
$$C_6F_5Br + BuLi \rightarrow C_6F_5Li \xrightarrow{C_6F_4} 2\text{-}LiC_6F_4C_6F_5$$

$$\xrightarrow[\text{with } 1,2-Br_2C_6F_4]{Li-Br\text{ exchange}} 2\text{-}BrC_6F_4C_6F_5 + 1\text{-}Li\text{-}2\text{-}Br\text{-}C_6F_4$$

The two main products of the reaction (formed in about 10% yield based on the total amount of 1,2-dibromotetrafluorobenzene initially added to the reaction vessel without taking into account the comparatively large quantities of 1,2-dibromotetrafluorobenzene remaining after the reaction) were isolated by large-scale vapour phase chromatography and shown by analysis to be isomeric tribromoheptafluorobiphenyls. Mass spectral analysis was of little value in deducing the structures of the isomers except that precise molecular weights were obtained; the bromine atoms were the groups most readily lost in a step-wise fashion on fragmentation of the molecules as was expected to be the case from the mass spectral study previously carried out on the 2-halononafluorobiphenyls[4]. The ^{19}F nuclear magnetic resonance spectra of the molecules dissolved in carbon tetrachloride could readily be understood in terms of the isomers 2,6,2'-tribromoheptafluorobiphenyl (I) and 2,3,2'-tribromoheptafluorobiphenyl (II):



(I)



(II)

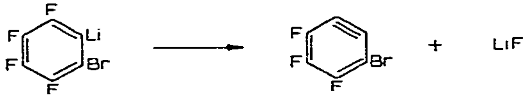
(I) was eluted from the VPC column a few minutes ahead of (II) in agreement with our previous observations on isomers containing 2- or 3-substituted biphenyls; biphenyls substituted in the 3-position are eluted more slowly than their 2-substituted counterparts. The ^{19}F nuclear magnetic resonance spectrum of (I) was characterised by the presence of a sharp doublet to lowest field which had an intensity twice that of other peaks in the spectrum and could therefore only arise from the two equivalent fluorine atoms F_3 and F_5 (split into a doublet by F_4) since these are the only two equivalent fluorine atoms in either isomer; the low-field position of this doublet also indicates that the fluorine atoms are both *ortho* to bromine atoms[4,6] which is further evidence for the correctness of the assignment. The chemical shifts of the various fluorine atoms are given in Table 1.

TABLE 1

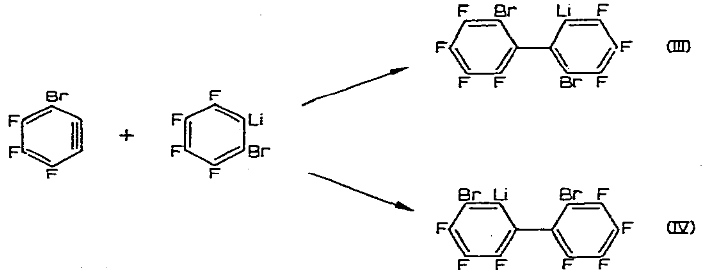
FLUORINE-19 NMR CHEMICAL SHIFTS OBSERVED FOR THE 2,6,2'- AND 2,3,2'-TRIBROMOHEPTAFLUOROBIPHENYLS (± 1 PPM RELATIVE TO CCl_3F)

	F'_3	F'_4	F'_5	F'_6	F_3	F_4	F_5	F_6
2,6,2'-$Br_3C_6F_4C_6F_3$	133.5	157.4	161.2	141.1	127.0	156.8	127.0	—
2,3,2'-$Br_3C_6F_4C_6F_3$	132.8	156.2	160.4	139.7	—	118.6	160.9	134.0

The formation of (I) and (II) can be explained by assuming that, during the thermal decomposition of 1-lithio-2-bromotetrafluorobenzene, bromotrifluorobenzyne is produced by the elimination of lithium fluoride:

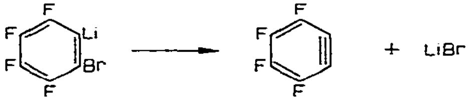


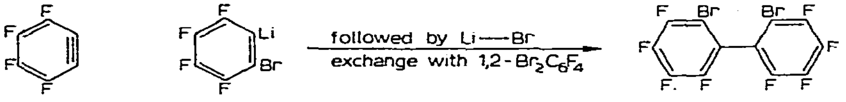
and that bromotrifluorobenzyne then adds on a molecule of undecomposed 1-lithio-2-bromotetrafluorobenzene, a process which can occur in two ways:



The final step in the mechanism is then proposed to be a lithium–bromine exchange between (III) or (IV) and 1,2-dibromotetrafluorobenzene to give (I) and (II) (we have previously demonstrated that such an exchange occurs between 2-lithiononafluorobiphenyl and bromopentafluorobenzene). The amounts of (I) and (II) formed are roughly equal and it would seem, therefore, that the addition of 1-lithio-2-bromotetrafluorobenzene to bromotrifluorobenzyne occurs in a purely statistical manner. The formation of bromotrifluorobenzyne as the main product in the decomposition of 1-lithio-2-bromotetrafluorobenzene is probably not surprising since the lattice energy of lithium fluoride is so much higher than that of lithium bromide; however, the position is complicated by the fact that under certain conditions tetrafluorobenzyne, once formed, will actually add a molecule of lithium bromide across the triple bond[5].

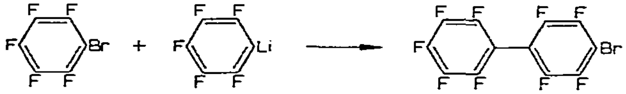
The presence of 2,2'-dibromooctafluorobiphenyl among the reaction products suggests that some tetrafluorobenzyne is formed during the decomposition of 1-lithio-2-bromotetrafluorobenzene (the quantities of 2,2'-dibromooctafluorobiphenyl and 2-bromononafluorobiphenyl are too large for them to have arisen completely from tetrafluorobenzyne formed by thermal decomposition of any pentafluorophenyllithium impurity).



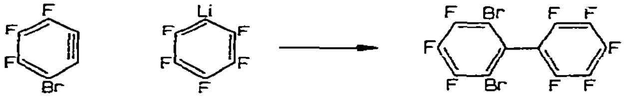


(V)

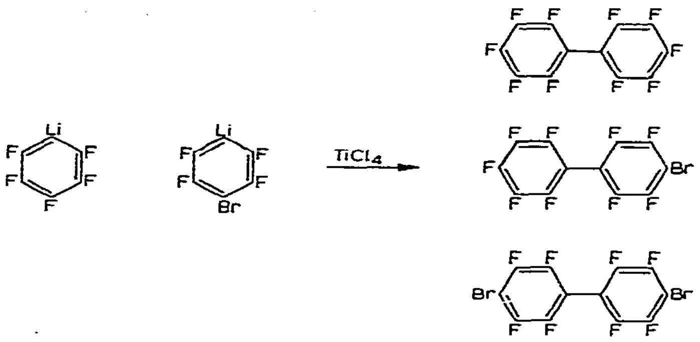
Apparently hydrolysis of the organolithium intermediates occurs to a small extent as evidenced by the appearance of hydro derivatives in trace quantities among the reaction products. The minute amounts of $C_{18}F_{10}Br_4$ and $C_{18}F_{11}Br_3$ detected mass spectrometrically can be explained by lithiation reactions occurring among the polybromobiphenyls in solution, followed by lithium fluoride elimination and addition of 1-lithio-2-bromotetrafluorobenzene to the substituted benzynes so produced. The only *definite* example we noted of a nucleophilic substitution product being formed was 4-bromononafluorobiphenyl which occurs in sufficiently small amounts to have arisen by the reaction



To check the influence of pentafluorophenyllithium impurity on the reaction, we carried out the decomposition of pentafluorophenyllithium in the presence of 1,2-dibromotetrafluorobenzene although, as shown in the *Experimental Section*, lithium-bromine exchange occurs at room temperature to give some 1-lithio-2-bromotetrafluorobenzene which complicates the result somewhat by forming, for example, 2,6-dibromooctafluorobiphenyl, but the other products formed in this reaction are in agreement with the reaction schemes suggested above. (We did not identify the other expected product, 2,3-dibromooctafluorobiphenyl.)



Several of the products of these benzyne reactions were also synthesised for comparative purposes using the titanium tetrachloride coupling reaction which we have briefly reported previously[7]. Since reporting the initial work on this coupling reaction we have altered the experimental procedure slightly and, as shown in the case of 2,2′-dibromooctafluorobiphenyl, the yields of pure product have been raised to over 80% of the theoretical; the coupling reaction can also be used to prepare 3,3′- and 4,4′-disubstituted octafluorobiphenyls. By carrying out "mixed" coupling reactions we have found the method very useful in synthesising many hydro- and bromo-substituted polyfluorobiphenyls, -terphenyls and -quaterphenyls[8]. This is illustrated by the synthesis of 4-bromononafluorobiphenyl:



where each component can be isolated in 15–20% yield by vapour phase chromatography.

SUMMARY

The decomposition of 1-lithio-2-bromotetrafluorobenzene in the presence of an excess of 1,2-dibromotetrafluorobenzene gives mainly a mixture of 2,3,2′- and 2,6,2′-tribromoheptafluorobiphenyls; several other products were also identified. 2,2′-Dibromooctafluorobiphenyl is formed in 88% yield when 1-lithio-2-bromotetrafluorobenzene is treated with an excess of titanium tetrachloride.

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