PERFLUOROPHENYL DERIVATIVES OF THE ELEMENTS XIV*. THE THERMAL DECOMPOSITION OF 2-LITHIONONAFLUORO-BIPHENYL

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There is a substantial body of evidence[2] to show that pentafluorophenyllithium readily loses lithium fluoride at temperatures around 0° to generate tetrafluorobenzyne, which can be trapped by the addition of, for example, lithium salts or benzene to the system:
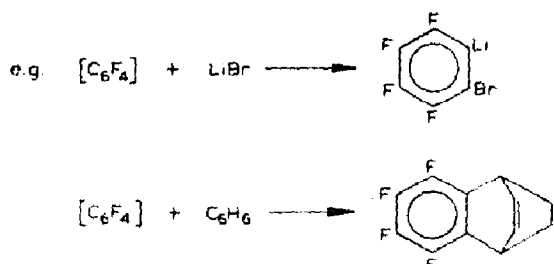
In the absence of such reagents tetrafluorobenzyne will add on a molecule of un-decomposed pentafluorophenyllithium to give 2-lithiononafluorobiphenyl which can be detected by the addition of water to the system and isolation of the hydrolysis product 2-hydrononafluorobiphenyl[2b].

During the decomposition of pentafluorophenyllithium in the presence of benzene[2d] we obtained as a by-product 1-pentafluorophenyl-2,3,4-trifluorobenzo-bicyclo[2.2.2]octatriene, thought to be formed from 1-pentafluorophenyl-2,3,4-trifluorobenzyne:

(I)
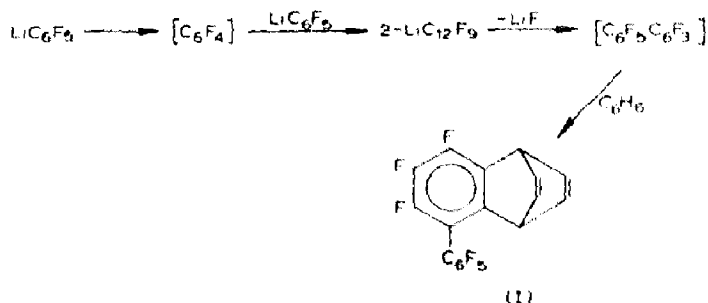
* For Part XIII see ref. 1.

We have now shown that the same product is obtained when 2-lithiononafluoro-biphenyl decomposes at about 0° in the presence of benzene, thus supporting the above reaction scheme. On heating to 300° in a sealed tube (I) loses acetylene to give 1-pentafluorophenyl-2,3,4-trifluoronaphthalene, identified by both elemental analysis and its mass spectrum.

In agreement with its structure, (I) has a proton NMR spectrum consisting of three groups of lines in intensity ratio 4:1:1 (at 6.9, 5.35 and 4.65 ppm from TMS respectively). The group of intensity four arises from the four (almost) equivalent olefinic protons; the other two groups, having chemical shifts expected for tertiary protons, are due to the inequivalent protons H_1 and H_4. Six groups of lines occur in
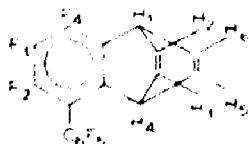

the ^{19}F NMR spectrum, two groups of which are twice the intensity of the other four; a reasonably large trans-annular coupling of about 6 cps occurs between F_2 and the *ortho* fluorines in the C_6F_5 ring.

The olefinic bonds in (I) should be favourably positioned for bonding to metals and on investigating this by refluxing (I) with an equimolar quantity of triiron dodecacarbonyl in petrol ether we were able to isolate 1-pentafluorophenyl-2,3,4-trifluorobenzobicyclo[2.2.2]octatrieneiron tricarbonyl (II) in about 20% yield.

We looked very closely at the decomposition of 2-lithiononafluorobiphenyl in an effort to detect the presence of the rather volatile perfluorobiphenylene[3] but apparently none is formed in the reaction; thus, as suggested by Tatlow[2a], the intra-molecular decomposition proceeds only by path (1):
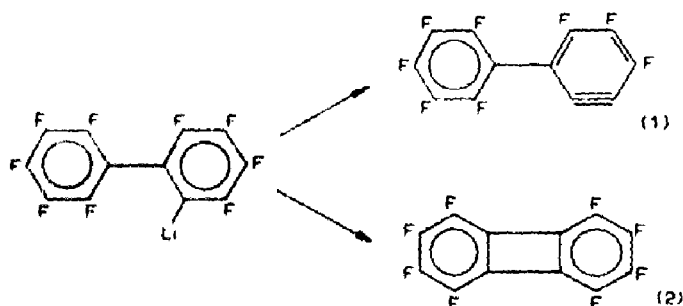
Having established that 2-lithiononafluorobiphenyl can lose lithium fluoride within the same ring to form a benzyne derivative, the decomposition of penta-fluorophenyllithium was allowed to occur in the presence of 2-hydrononafluoro-biphenyl. It was hoped that any 1-pentafluorophenyl-2,3,4-trifluorobenzyne, formed as an intermediate, would add undecomposed pentafluorophenyllithium to give the terphenyl derivatives (III) and (IV), and that these would undergo lithium–hydrogen exchange with the 2-hydrononafluorobiphenyl in the same way that 2-lithionona-fluorobiphenyl exchanges with the *single* ring compound pentafluorobenzene[2]:
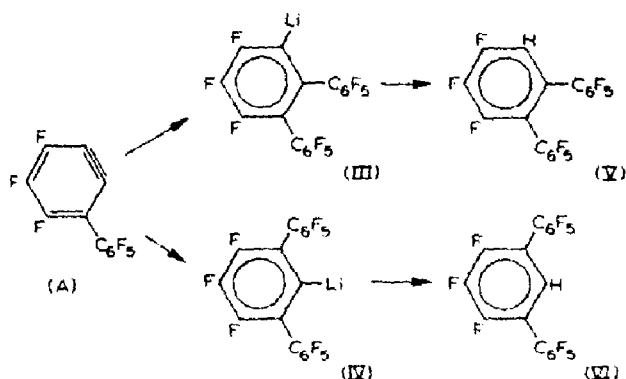
The hope was apparently justified since after four days at room temperature it was possible to isolate (V) (m.p. 90–92°) and (VI) (m.p. 113.5–115°) from the mixture in 15 % total yield, about 90 % being (V). The compounds (V) and (VI) proved identical to two terphenyls which had previously been isolated in very low yield from experiments involving the addition of an *excess* of pentafluorophenyllithium to metal chlorides where the mixtures had been held at room temperature for some hours before hydrolysis. This demonstrates that the terphenyl system is built up during the thermal decomposition of pentafluorophenyllithium and does not require the deliberately added presence of 2-hydrononafluorobiphenyl. In this latter system, however, the proportion of terphenyls obtained is about 75 % (VI): 25 % (V). It is suggested that this is because in the absence of 2-hydrononafluorobiphenyl, (III) can undergo further loss of lithium fluoride and addition of pentafluorophenyllithium to give quaterphenyls, whereas (IV) cannot undergo further reactions in this manner. The conversion of the benzyne (A) via (III) to (V) would seem to be more favourable than that of (A) via (IV) to (VI), resulting in (V) being formed as the major component in the presence of 2-hydrononafluorobiphenyl. However, in systems where no Li–H exchange is possible until the final hydrolysis, (VI) is the major product owing to the less reactive nature of intermediate (IV). As in the biphenyl system, if pentafluorobromobenzene from the preparation of C_6F_5Li is fortuitiously present in the reaction mixture then Li–Br exchange can occur with (III) and (IV) and, for example, traces of 1,3-bis(pentafluorophenyl-2-bromo-4,5,6-trifluorobenzene (VIII, m.p. 99–101°) can be isolated by vapour phase chromatography from such mixtures.

The structure of (V) was deduced from its ^{19}F NMR spectrum which showed the expected nine groups of lines of approximate intensities (1 : 1) : 2 : 2 : 1 : 1 : 1 : 4, field increasing to the right; the "group" of intensity 4 was caused by *partial* overlap of the resonances due to the meta fluorine atoms in each C_6F_5 ring. The proton NMR spectrum of (VI) dissolved in carbon tetrachloride consisted of a triplet ($\delta = 7.05$ ppm from TMS, J(H–F) 6.8 cps due to coupling of the proton with the two fluorines meta to it, each component being split into a doublet (J(H–F) 2.6 cps) by the fluorine atom para to the proton; due to the symmetrical nature of the molecule, the ^{19}F NMR spectrum of (VI) is relatively simple and consists of five groups of lines only.

On repeating the above experiment in the presence of 2-bromononafluorobiphenyl instead of 2-hydrononafluorobiphenyl, the intermediate lithio derivatives (III) and (IV) undergo Li–Br exchange giving 1,2-bis(pentafluorophenyl)-3-bromotrifluorobenzene (VII, m.p. 102–104°) and 1,3-bis(pentafluorophenyl)-2-bromotri-

TABLE 1A

^{19}F NMR CHEMICAL SHIFTS IN THE TERPHENYLS RECORDED AT 94.1 Mc

(V, X=H ; VII, X=Br)

(VI, X=H ; VIII, X=Br)
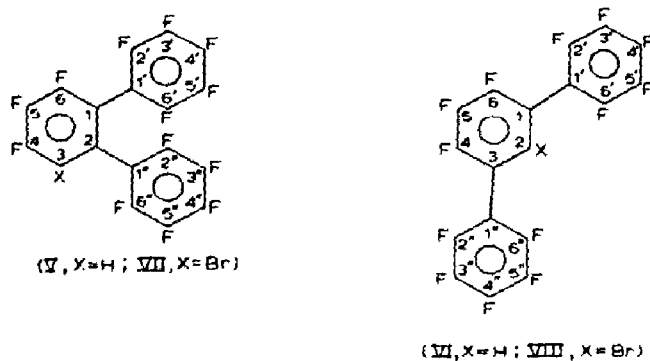
Terphenyls	Fluorine atom positions								
	4	5	6	2',6'	(2",6")	3',5'	(3",5")	4'	(4")
(V)	129.7	155.2	129.5	139.3	141.2	160.5	160.7	150.5	151.4
(VII)	116.9	151.7	130.3	138.7		160.5	160.6	150.1	150.4
(VI)	128.8	154.8	128.8	140.6		161.4		152.2	
(VIII)	124.6	156.2	124.6	138.2		161.1		150.9	

TABLE 1B

^{1}H NMR CHEMICAL SHIFTS AND COUPLING CONSTANTS RECORDED AT 100 Mc

Terphenyls	Chemical shifts (ppm from TMS)	Coupling constants (cps)			
		$J(H-F_4)$	$J(H-F_5)$	$J(H-F_6)$	$J(H-F_{2',6'})$
(V)	7.05	9.6	6.6	1.3	0.7
(VI)	7.05	6.8	2.6	6.8	0.8

TABLE 2

COUPLING CONSTANTS FROM THE ^{19}F NMR SPECTRA OF THE TERPHENYLS RECORDED AT 94.1 Mc

x–y		Coupling constants $J(F_x-F_y)$ (cps) in			
		(V)	(VII)	(VI)	(VIII)
4–5		20.4	20.8	19.8	21.0
4–6		10.3	10.4		
5–6		20.4	20.8	19.8	21.0
3'–4',	3"–4"	20.0, 20.2	20.1, 20.4	20.0	20.0
2'–3',	2"–3"	±22.0, 21.8		22.0	21.9
2'–5',	2"–5"	∓8.5, ±8.2		±8.5	±8.2
2'–6',	2"–6"	4.0 3.9		3.7	5.6
3'–5',	3"–5"	0.9 0.8		0.9	1.6
2'–4',	2"–4"	1.2 1.5	2.5, 2.7	2.4	2.9
4–2',6'				3.5	1.8
6–2',6'		5.0	4.2	3.5	1.8

fluorobenzene, (VIII); the ratio of (VII)/(VIII) is approximately 4 : 1. Lithiation of (VII) [or (VIII)] using butyllithium at low temperature followed by hydrolysis yields (V) [or (VI)] while bromination in oleum converts (V) back to the bromo-derivative (VII).

x = H (V)
x = Br (VII)

x = H (VI)
x = Br (VIII)
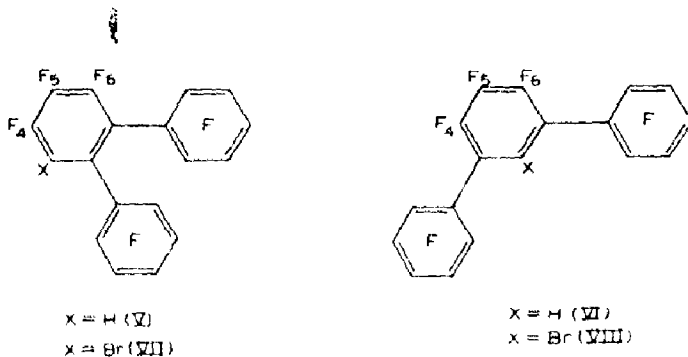
The ^{19}F NMR spectrum of (VIII) dissolved in $CHCl_3-CFCl_3$ consists of 5 groups of lines, three of which are due to the *ortho, meta* and *para* fluorine atoms of the identical pentafluorophenyl groups. Of the remaining two groups, that at higher field is due to F_5 and consists of a triplet due to splitting by F_4 and F_6; the group at lower field is due to F_4 and F_6 and is a doublet from coupling with F_5, with further triplet structure due to splitting by the *ortho* fluorines of the neighbouring penta-fluorophenyl rings (one next to F_4 and one next to F_6). The ^{19}F NMR spectrum of (VII) is rather more complicated due to partial overlap of the groups of lines due to the fluorines of the two pentafluorophenyl groups which are not now identical. A combination of the use of substitution parameters and coupling constants evaluated from the spectra obtained enable complete understanding on the basis of the suggested structures of the four terphenyls; the peak assignments and chemical shifts are given in Table 1A and coupling constants in Table 2.

By a careful work-up of the products formed during the preparation of 2-bromononafluorobiphenyl from pentafluorophenyllithium[2] we have been able to increase the yield of 2-$BrC_{12}F_9$ from about 30 % to 75 %; from among the other products we isolated two mono-bromoperfluoroterphenyls (overall yield *ca.* 8 %) one of which proved identical to (VII).

Intramolecular loss of lithium fluoride by (III) to give bis(pentafluorophenyl)-difluorobenzyne followed by addition of undecomposed pentafluorophenyllithium is possible[4] and we are studying this reaction further at the present time.

EXPERIMENTAL

Reactions were carried out under an atmosphere of dry, oxygen-free nitrogen; analyses were performed by Dr. A. Bernhardt, Mülheim, Ruhr. We are grateful to the Imperial Smelting Corporation Ltd., for gifts of fluoro-aromatic derivatives. The preparation of 2-hydrononafluorobiphenyl has been described previously[2b,2c].

Decomposition of 2-lithiononafluorobiphenyl in the presence of benzene
2-Lithiononafluorobiphenyl (prepared from 2-bromononafluorobiphenyl, 2 g,

and n-butyllithium, 4 ml of 2.45 molar solution in hexane) was allowed to stand at 0° for 4 h in the presence of benzene (125 ml). Removal of the solvent under vacuum followed by vacuum sublimation gave 1-pentafluorophenyl-2,3,4-trifluorobenzo-bicyclo[2,2,2]octatriene (I), m.p. 171–173°, identical to the sample we had previously prepared from pentafluorophenyllithium[2d]. A further check on the identity was obtained from the mass spectrum which showed a parent ion at $m/e = 374$ with a doubly charged parent ion at $m/e = 187$.

On being heated in a sealed tube under vacuum to 280° (I) lost acetylene to give 1-pentafluorophenyl-2,3,4-trifluoronaphthalene, m.p. 122–124°. (Found: C, 55.3; H, 1.3; F, 43.5; $m/e = 348$. $C_{16}H_4F_8$ calcd.: C, 55.2; H, 1.2; F, 43.6%; mol.wt., 348.)

Reaction of (I) with triiron dodecacarbonyl

A solution of (I), 0.36 g, and triiron dodecacarbonyl, 0.16 g, in 100–120° petrol ether (100 ml) were refluxed for 4 h when the green colour of the iron carbonyl was displaced. The solvent was removed under vacuum and the 1-pentafluorophenyl-2,3,4-trifluorobenzobicyclo[2,2,2]octatrieneiron tricarbonyl product, m.p. 122–125°, was purified by recrystallization from 40–60° petrol ether. (Found: C, 49.35; H, 1.1; F, 30.0. $C_{21}H_6F_8FeO_3$ calcd.: C, 49.05; H, 1.2; F, 29.6%.)

Decomposition of pentafluorophenyllithium in the presence of 2-hydrononafluorobiphenyl

2-Hydrononafluorobiphenyl, 1.2 g and pentafluorophenyllithium (from penta-fluorobenzene, 2.5 g and butyllithium, 5.8 ml of 2.7 molar solution in hexane) were stirred at room temperature in 100 ml of dry ether for 96 h. The solvent was removed and part of the remaining 2-hydrononafluorobiphenyl sublimed away at room temperature and 10^{-4} mm. Vacuum sublimation at 140° followed by GLC on a silicone column afforded analytical samples of the terphenyls (V) (m.p. 90–92°, 310 mg) and (VI) (m.p. 113.5–115°, 40 mg). (Found for (V): C, 46.8; H, 0.22; F, 53.3; for (VI): C, 46.6; H, 0.17; F, 53.3. $C_{18}HF_{13}$ calcd.: C, 46.6; H, 0.22; F, 53.2%.) Their molecular weights were checked by mass spectroscopy which gave $m/e = 464$ for both samples; their cracking patterns were rather similar with the fragment $(P–CF_3)^+$ having the highest intensity, apart from P^+, in each case. The two terphenyls are also isolated, but in low yield, from the decomposition of pentafluorophenyllithium in ether–hexane solvent mixtures in the absence of 2-hydrononafluorobiphenyl.

Decomposition of pentafluorophenyllithium in the presence of 2-bromononafluorobiphenyl

n-Butyllithium (9.5 ml of 2.7 molar hexane solution) was added to bromo-pentafluorobenzene (6.2 g) in ether (75 ml) at −78° and stirred for three-quarters of an hour. 2-Bromononafluorobiphenyl (3.3 g) in ether (50 ml) was added and the mixture allowed to reach room temperature and stirring continued for 48 h. Removal of solvent gave a yellow-brown solid; addition of pentane followed by filtration and removal of pentane gave a yellow-brown viscous liquid. Analytical vapour phase chromatography (GLC) indicated the presence of unreacted bromopentafluorobenzene and 2-bromo-nonafluorobiphenyl, 2-hydrononafluorobiphenyl, 1,2-bis(pentafluorophenyl)-4,5,6-trifluorobenzene and two compounds (ratio 4.1:1) of longer retention times. These were isolated by preparative scale GLC (silicone column) the first to elute being 1,2-bis(pentafluorophenyl)-3-bromotrifluorobenzene, m.p. 102–104°. (Found: C, 39.7; H, 0.1; Br, 14.7; F, 45.2. $C_{18}BrF_{13}$ calcd.: C, 39.8; H, 0.0; Br, 14.7; F, 45.5%.) The

second component was 1,3-bis(pentafluorophenyl)-2-bromotrifluorobenzene, m.p. 99–101° (analysed by its mass spectrum).

Preparation of 2-bromononafluorobiphenyl

n-Butyllithium (19 ml of 2.7 molar hexane solution) was added to bromopentafluorobenzene (24.7 g) in ether (125 ml) at −78° and stirred for 20 min; the mixture was then stirred for a further 18 h at room temperature. Removal of solvent followed by vacuum sublimation, 60–70° (10^{-4} mm) gave a white crystalline solid which had identical melting point, infrared spectrum and GLC retention time to 2-bromononafluorobiphenyl. Yield 14.6 g (75%).

Further vacuum sublimation at 120° gave 0.85 g of a tacky white solid, shown by preparative GLC to consist of further 2-bromononafluorobiphenyl, 1,2-bis-(pentafluorophenyl)-3-bromotrifluorobenzene and an unidentified bromoperfluoroterphenyl, m.p. 109–112°, (apparently containing only one pentafluorophenyl ring from the ^{19}F NMR spectrum). (Found: C, 40.0; H, 0.1; Br, 15.6; F, 44.5. $C_{18}BrF_{13}$ calcd.: C, 39.8; H, 0.0; Br, 14.7; F, 45.5%.)

IR spectra (recorded as mulls in nujol and hexachlorobutadiene)

(V): 2930 w, 2920 w, 1655 m, 1636 m, 1612 m, 1591 w, 1526 m(sh), 1515 s, 1503 s, 1495 s(sh), 1475 m, 1449 vw, 1416 w, 1387 m, 1360 w, 1342 vw, 1324 vw, 1298 w, 1255 w, 1196 w, 1152 w, 1099 s, 1070 s, 1046 vw, 1015 m(sh), 1010 m, 992 s, 947 vw, 930 w, 888 vw, 869 m, 866 w(sh), 829 vw, 799 m, 783 w, 768 vw, 754 w, 740 w, 724 w, 713 s, 668 vw, 625 m, 580 w, 562 w.

(VI): 2959 vw, 2928 w, 1656 w, 1639 vw, 1629 vw, 1621 w, 1522 s, 1499 vs, 1490 s(sh), 1471 m, 1420 vw, 1405 vw, 1389 w(sh), 1383 w, 1319 vw, 1299 vw, 1276 w, 1264 w, 1247 w, 1156 w, 1109 s, 1099 w, 1071 w, 1052 vs, 1037 w, 1010 w(sh), 995 vs, 931 w, 899 m, 870 vw, 784 m, 757 vw, 741 w, 723 w, 714 w, 704 m, 686 w, 669 vw, 662 vw, 652 m(sh), 649 m, 597 vw, 575 w, 570 w.

(VII): 1661 m, 1621 m, 1610 w, 1592 w, 1531 s, 1511 s(sh), 1499 s, 1490 s, 1473 s, 1466 m(sh), 1451 m, 1414 m, 1292 m, 1264 w(sh), 1252 m, 1151 w, 1112 s, 1109 m(sh), 1076 s, 1043 w, 1016 s, 997 s(sh), 989 s, 983 s(sh), 945 m, 850 m, 741 w, 720 s, 709 w, 672 m, 671 m(sh), 660 w, 629 m, 580 w.

(VIII): 1661 w, 1623 w, 1531 m, 1513 s(sh), 1508 s, 1484 s, 1477 s, 1460 s(sh), 1414 w, 1290 w, 1264 w, 1147 w, 1129 w, 1122 m, 1112 m, 1074 s, 1018 m, 997 s, 988 s, 983 s(sh), 941 m, 833 m, 769 m, 718 w, 709 w, 667 w, 650 m.

SUMMARY

2-Lithiononafluorobiphenyl in ether/hexane solvent mixtures has been shown to lose lithium fluoride giving 1-pentafluorophenyl-2,3,4-trifluorobenzyne which was detected by the formation of addition compounds with benzene and pentafluorophenyllithium.

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