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AROMATIC POLYFLUOROCOMPOUNDS—XLIII[1]

REACTIONS OF TETRAFLUOROBENZYNE WITH AROMATIC AND HETEROAROMATIC COMPOUNDS

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Abstract—Tetrafluorobenzyne reacts with benzene, toluene, the isomeric xylenes, durene, thiophen, 1-methylpyrrole, cyclopentadiene and styrene to give Diels-Alder type adducts. In the cases where mixtures of isomers formed these have been separated and their ratios determined. The further chemistry of some of the adducts is described.

IN PREVIOUS papers[2,3] we have described the formation and some of the reactions of tetrafluorobenzyne and the present results have been reported as a preliminary communication.[4] There are many examples of the reactions of benzyne with olefinic and aromatic substrates[5] to give Diels-Alder adducts usually in low yield. However, since we have shown[2] that furan reacts with tetrafluorobenzyne to give a good yield of adduct, reactions of the aryne with less activated substrates were investigated.

Pentafluorophenyl lithium was prepared as previously described[3] in ether and was allowed to decompose in the presence of excess benzene. Under these conditions three products were formed. Separation by a combination of gas chromatography, column chromatography and vacuum sublimation yielded pure components, which were shown by analysis, mass spectrometry and spectroscopy and comparison with authentic samples to be 2,*H*-nonafluorobiphenyl[3] 2,3-[tetrafluorobenzo]bicyclo-[2.2.2]octatriene (I) and an eicosafluoroquinquephenyl. The octatriene had correct analysis and top mass peak corresponding to the molecular ion in its mass spectrum. Its ^{1}H NMR spectrum showed two groups of peaks at 4·73 γ and 3·14 γ corresponding to the halves of an A_4X_2 type system which could be analysed as two A_2X_2 systems since in all cases we have studied there appears to be no cross ring coupling between the bridgehead protons i.e. $J_{xx} = 0$ and further there appeared to be no coupling between corresponding olefinic protons in each half of the A_4X_2 system. The ^{19}F spectrum showed a typical A_2X_2 system previously characterised for the furan adduct, a more detailed analysis of the ^{19}F spectra will be published elsewhere.[6]

Pyrolysis of the adduct in a sealed tube at 300° or in a flow system at 450° afforded 1,2,3,4-tetrafluoronaphthalene[2] and acetylene identified by their IR spectra. The octatriene has been prepared by other workers synchronously with and subsequently to our original communication. It was erroneously described as a biphenyl by Vorozhtsov[7] a result subsequently corrected[8a] and by Heaney and Brewer[9] using pentafluorophenyl magnesium halides as the benzyne source and by Massey[10] using the lithium route.

The quinquephenyl was also observed by Massey who mainly on the basis of ^{19}F NMR suggests the compound to be the result of successive benzyne reactions.

The possibility of nucleophilic substitution of the first formed 2*H*-nonafluorobiphenyl cannot however be excluded in view of the rapid reaction of decafluorobiphenyl with pentafluorophenyl lithium to yield polyphenyls.[3] Work on the orientation of substitution of 2H-nonafluorobiphenyl is in progress to attempt to resolve this problem.[12]

We have found that solvent plays a very important part in this reaction. Under the conditions described above, the biphenyl and the quinque phenyl were the major products, but if the reaction is carried out in pure benzene or benzene/hexane mixtures the octatriene is produced exclusively and in good yield.

These results along with others we have obtained[13] suggest that nucleophilic displacement reactions will occur in preference to benzyne reactions where possible. This is probably due to the difference in aggregation of organolithium reagents in polar and non polar solvents facilitating or hindering ionic type reactions.

With this solvent effect in mind all of our subsequent reactions were carried out under the best conditions in hydrocarbon solvents. Toluene reacted smoothly with tetrafluorobenzyne to give a mixture of two products in the ratio 87:13 as shown by gas chromatography. The major product was shown by mass spectrometry, analysis and NMR spectroscopy to be 2-methyl-5,6-[tetrafluorobenzo]-bicyclo[2.2.2]-octatriene (III). The 'H NMR spectrum showed five groups of peaks in the integral ratio of 2:1:1-1:3 consistent with the proposed structure (for analysis of spectra see later). The minor component was similarly shown to be 1-methyl-2,3-tetrafluorobenzobicyclo[2.2.2]octatriene (II). The 'H NMR spectrum consisted of four groups of peaks in the integral ratio of 2:2:1:3 and can readily be analysed as an ABX system. Pyrolysis of II afforded 1,2,3,4-tetrafluoro-5-methylnaphthalene, identical with an authentic sample prepared unambiguously.[12] In a recent paper the same compounds have been obtained in apparently an inverse ratio[8a] a result seemingly due to typographical error.[8b] In a similar reaction with *o*-xylene two products in the ratio 61:39 were obtained. The major component was shown to be 2,3 dimethyl-5,6-[tetrafluorobenzo] bicyclo[2.2.2] octatriene (IV) and the minor product 1,2-dimethyl 5,6-[tetrafluorobenzo] bicyclo[2.2.2] octatriene (V). The 'H NMR spectrum of IV showed three groups of peaks in the ratio 2:2:3 and the first groups consisted of an A_2X_2 type the A band of which could be easily analysed by standard methods, the band due to the proton $H_xH_{x'}$ was in this spectrum and others of similar type complicated by H to F coupling to adjacent fluorine atoms. The 'H NMR spectrum of V was complex but could be analysed.

Reaction with *m*-xylene afforded similarly two products in the ratio of 64:36. The major component was shown to be 2,7-dimethyl-5,6-[tetrafluorobenzo] bicyclo[2.2.2] octatriene (VI). The 'H NMR spectrum showed four groups of peaks in the ratio 2:1:1:3 which could be simply analysed by first order analysis. The minor component was shown to be 1,5-dimethyl-2,3-[tetrafluorobenzo] bicyclo-[2.2.2] octatriene (VII). The 'H NMR spectrum was more complex containing a ABX system and a simple olefinic proton. It was found possible to analyse the AB part of the ABX system and also the olefin part separately.

p-Xylene reacted smoothly to give a single component which was shown by analysis of the 'H NMR spectrum to be the compound with the Me group off the bridgehead position namely 2,5-dimethyl-7,8,[tetrafluorobenzo] bicyclo[2.2.2] octatriene (VIII). No evidence for the compound with the Me groups on the bridgehead could be found. Reaction with durene similarly gave a single component with a very simple ^{1}H NMR spectrum clearly attributable to the compound being 2,3,5,6-tetramethyl-7,8-[tetrafluorobenzo] bicyclo[2.2.2] octatriene (IX).

An interesting feature of these results is the preponderance of the isomers in which Me groups are situated off the bridgehead positions; similar observations have been made in Diels-Alder reactions of cyanoacetylenes with aromatic compounds.[14] A possible explanation of our results is that the attack of the benzyne is a two step process, the first step being an electrophilic attack as shown in Fig. 1. This type of reaction might be expected to lead to substitution patterns similar to those obtained in nitration. The results obtained compared with the literature values for nitration are shown in Table 1.[15] The values given in Table 1 clearly show some agreement but in the benzyne case there is a larger tendency towards ortho substitution. A second possibility is that the benzyne is behaving as a free radical as shown in Fig. 2, there orientation ratio is in good agreement with the toluene value[16] but no data is available for the xylenes, thus making a choice between the possibilities somewhat meaningless.

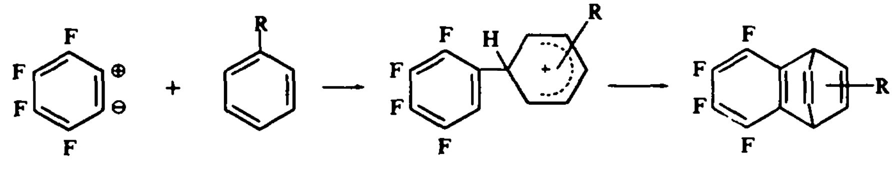

FIG. 1.

TABLE 1.

Substrate	% Nitration O.	P.	Isomers Bridgehead Me	Bridgehead H
Toluene	67	33	13	87
o-Xylene	58	42	38	62
m-Xylene	15	85	64	36
p-Xylene	100	0	0	100

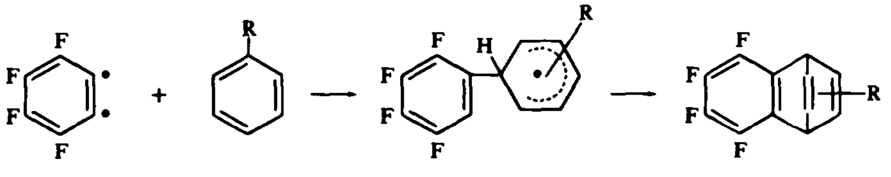

FIG. 2.

In view of the high reactivity of tetrafluorobenzyne with aromatic compounds a number of reactions with olefins which usually participate in Diels-Alder reactions were carried out. Thus reaction of the benzyne, generated either by the Grignard or lithun route, with styrene afforded a mixture of two products together with some non-fluorine containing low molecular weight polystyrene. The mixture was readily separated by a combination of column chromatography and distillation to yield a solid, shown by analysis, mass spectrometry and NMR spectroscopy to be 1,2,3,4-tetrafluoro-9, 10-diphydrophenanthrene (X). The second component a liquid was identified similarly as 1,2,3,4-tetrafluoro-9-β-phenylethyl 10-hydrophenanthrene (XI). The former product X is the expected Diels-Alder adduct whilst the latter is envisaged to arise by a reaction scheme such as that illustrated in Fig. 3. A similar pathway to this has been invoked to explain the formation of 9-phenyl-10-hydrophenanthrene from styrene and benzyne.[17]

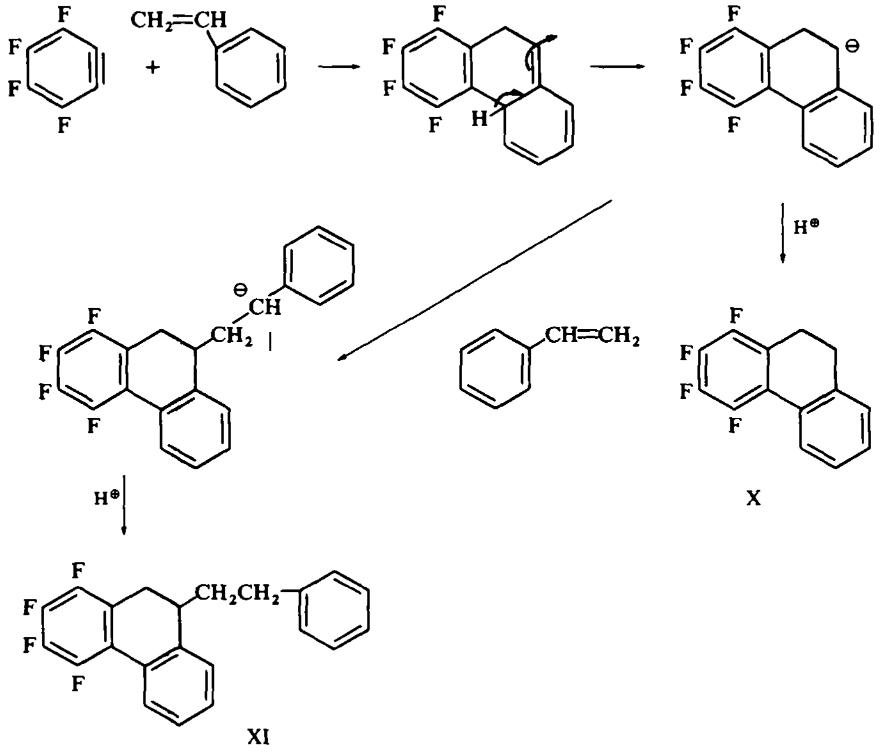

FIG. 3.

Treatment of X with Pd-C at 250° afforded 1,2,3,4-tetrafluorophenanthrene (XII) in good yield. Distillation of XI *in vacuo* afforded XI together with styrene and a similar result was obtained by heating with Pd-C at 250°.

Cyclopentadiene was found to react with tetrafluorobenzyne only at elevated temperatures at which presumably the rate of the reaction was greater than that of dimerization of cyclopentadiene. The expected product tetrafluorobenzobicycloheptadiene (XIII) was formed in moderate yield. Pyrolysis of the product at 280° afforded tetrafluoronaphthalene in excellent yield, no evidence for the formation

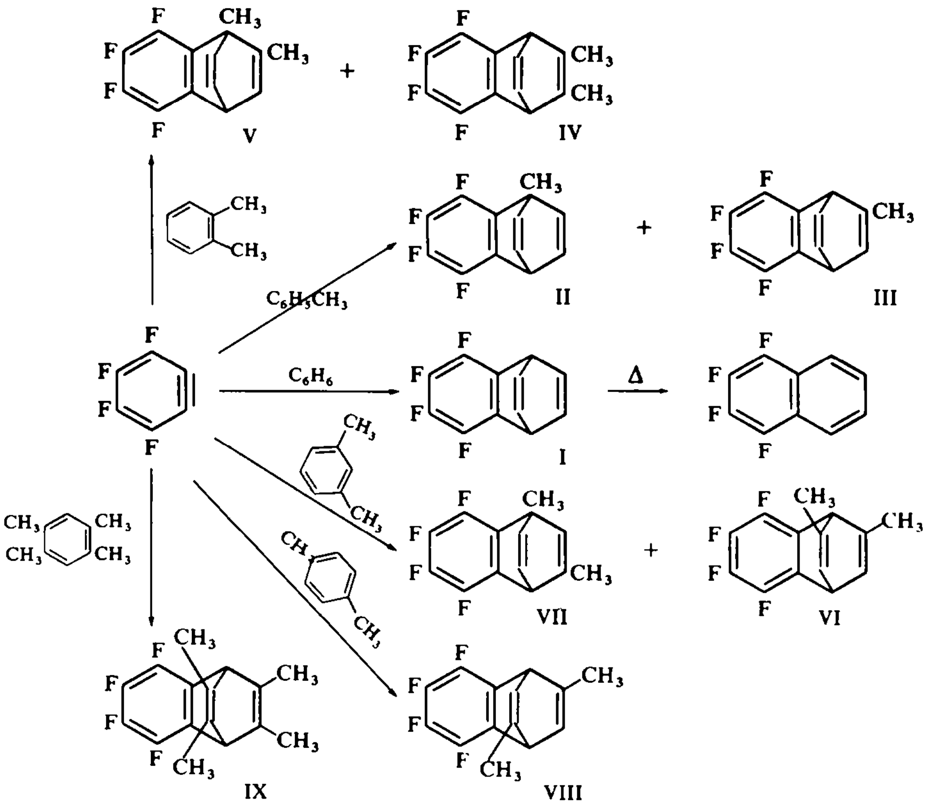
V
IV
II
III
I
VII
VI
IX
VIII
$C_6H_5CH_3$
C_6H_6
Δ

FIG. 4.

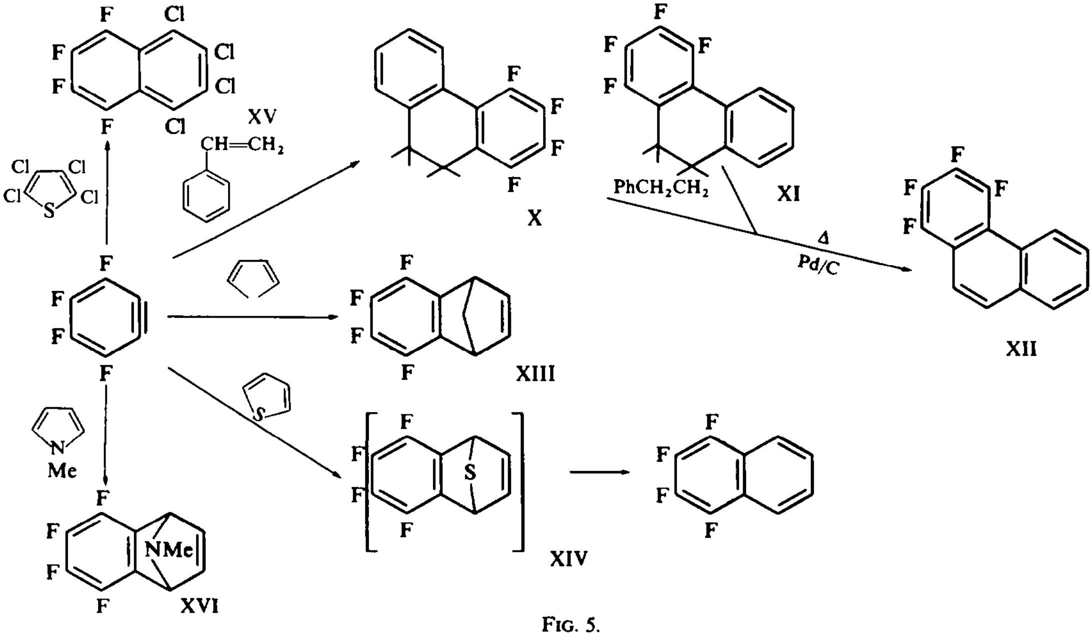
XV
X
XI
XII
XIII
XIV
XVI
PhCH₂CH₂
Δ
Pd/C
NMe
Me

FIG. 5.

of a benzocycloheptatriene; the product produced by pyrolysis of the corresponding hydrocarbon.[18] Reaction of the benzyne with pentafluorostyrene afforded a crystalline compound in quite good yield. The ^{19}F and $'H$ NMR spectra and the mass spectrum were consistent with the product being the expected adduct but even after many recrystallizations satisfactory analysis could not be obtained.

In spite of many attempts[19] Diels-Alder reactions of thiophen have hitherto not been reported. Tetrafluorobenzyne being a very reactive dienophile might be expected

TABLE 2. 'H NMR SPECTRA OF COMPOUNDS

Compound	Protons	Shifts γ units	Coupling constants c/s
$R_1 = R_2 = R_3 = R_4 = H$	6, 7, 8, 9, 10	3·1	$J_{78} = J_{89} = J_{56} = J_{510} = 6\cdot0$
(I)	5, 8	4·7	$J_{910} = J_{76} = 7\cdot0$
			$J_{810} = J_{59} = J_{76} = J_{68} = 1\cdot5$
$R_2 = R_3 = R_4 = H\ R_1 = Me$	5	4·7	$J_{9,10} = J_{67} = 6\cdot8$
(II)	6, 10	3·1	$J_{520} = J_{56} = 6\cdot0$
	7, 9	3·5	$J_{59} = J_{57} = 1\cdot8$
	Me	7·8	$J_{F_1-Me} = 5\cdot0$
$R_1 = R_3 = R_4 = H\ R_2 = Me$	9, 10	3·1	$J_{510} = J_{89} = 5\cdot8$
(III)	6	3·6	$J_{59} = J_{810} = 1\cdot5$
	8	4·8	$J_{56} = 6\cdot0$
	5	5·0	$J_{910} = 7\cdot0$
	Me	8	$J_{6-Me} = 2J_{68} = 1\cdot8$
$R_1 = R_4 = H\ R_2 = R_3 = Me$	9,10	3·2	$J_{89} = J_{510} = 5\cdot9$
(IV)	5, 8	5·1	$J_{810} = J_{59} = 1\cdot5\ J_{9-10} = 7\cdot0$
	Me	8·2	
$R_3 = R_4 = H\ R_1 = R_2 = Me$	9, 10, 6	2·9–3·6	$J_{510} = 6\cdot3\ J_{6Me} = 1\cdot8$
(V)	5	4·9	$J_{56} = 6\cdot2\ J_{MeF} = 5\cdot0$
	Me	8·3	$J_{59} = 1\cdot8$
	CMe	8·6	
$R_1 = R_2 = H\cdot R_3 = R_4 = Me$	7, 9	3·7	$J_{89} = J_{78} = 6\cdot0$
(VI)	8	5·1	$J_{7Me} = J_{9Me} = 1\cdot8$
	5	5·4	
	Me	8·1	$J_{18} = 2\,J_{45} = 1\cdot8$
$R_2 = R_4 = H\ R_1 = R_3 = Me$	10	3·2	$J_{910} = 6\cdot8\ J_{\dot{5}9} = 1\cdot7$
(VII)	9	3·5	
	7	4·0	$J_{510} = 5\cdot9\ J_{57} = 1\cdot7$
	5	5·2	
	Me(R_1)	8·0	$J_{7Me(R_3)} = 1\cdot8$
			$J_{F_1Me(R_1)} = 4\cdot9$
	Me(R_3)	8·1	
$R_1 = R_3 = H\ R_2 = R_4 = Me$	6, 9	3·7	$J_{89} = J_{56} = 6\cdot0$
(VIII)	5, 8	5·3	$J_{86} = J_{59} = 1\cdot8$
	Me	8·1	$J_{6Me} = J_{9Me} = 2\cdot0$
			$J_{18} = J_{45} = 1\ J_{15} = J_{48} = 1\cdot0$
Miscellaneous Compounds			
IX	1, 4	4·4	
	Me	7·8	
	58	5·76	$J_{78} = J_{56} = J_{68} = J_{57} = 2\cdot0$
	76	3·22	$J_{59} = J_{89} = 1\cdot3$
	9	7·78	$J_{18} = J_{43} = 1\ J_{13} = J_{48} = 1\cdot0$

to yield a 1:4 adduct with thiophen. It was found that reaction under the same conditions as those used for benzene afforded 1,2,3,4-tetrafluoronaphthalene as the major product in good yield. Careful separation of the mother liquors from the reaction, using alumina chromatography afforded a small quantity of pentafluorothiophenol. There seemed to be two possible interpretations of this result: either pentafluorophenyl lithium was causing desulphurization of the thiophen to generate a butadiene type compound *in situ* which further reacted to give the naphthalene or the unstable adduct (XIV) was formed which decomposes to the naphthalene and sulphur which then reacts by the known reaction[20] to give the thiophenol. In order to test these possibilities, thiophen was added to a cooled concentrated solution of pentafluorophenyl lithium in an NMR tube. The mixture was allowed to warm up inside the NMR machine. The initial peaks due to thiophen disappeared to be replaced by peaks at 2·9 and 4·1 γ attributable to the bridghead and olefinic protons in XIV. These peaks rapidly disappeared to give finally the typical AA'XX' peaks of tetrafluoronaphthalene. This evidence suggests that the unstable episulphide (XIV) could be an intermediate and that this reaction is a true 1:4 Diels-Alder reaction. Attempts to isolate the episulphide have so far been unsuccessful.

Reactions with thiophen derivatives take place in a similar manner e.g. 2-methyl thiophen affords 1,2,3,4-tetrafluoro-5-methylnaphthalene.[21] Reaction with tetrachlorothiophen afforded a small yield of 1,2,3,4-tetrachlorotetrafluoronaphthalene (XV).

TABLE 3. ^{19}F NMR C_6H_6/C_6F_4 (I)

F_1	F_2	F_3	F_4		
142·5	154·4	154·5	142·5		
J_{F,F_4}	J_{F,F_2}	J_{F,F_3}	$J_{F_2F_3}$	J_{F,F_4}	$J_{F_2F_4}$
18·3	23·5	0·5	15·8	23·5	0·5

There have been reports of reactions of pyrrole derivatives with benzyne[22] but unless the pyrrole is highly substituted further reaction occurs to give secondary products of the original adduct.[23] In view of the high reactivity of tetrafluorobenzyne with other aromatic systems some reactions with pyrroles were carried out. Pyrrole or potassium pyrrole gave only intractable tars using either the Grignard or lithium routes to tetrafluorobenzyne. 1-Methylpyrrole, however, reacted smoothly to give a high yield of the expected adduct 1,2,3,4-tetrafluoro-5-8-dihydro-5,8-N-methyliminonaphthalene (XVI) no evidence for further reaction was obtained. The adduct was stable under nitrogen in the dark, but rapidly darkened in air and light. Treatment of the adduct with aqueous or ethanolic acid afforded 1,2,3,4-tetrafluoro-5-N methylaminonaphthalene (XVII), identical to a sample prepared from 1,2,3,4-tetrafluoro-5-nitronaphthalene.[21] It has been shown recently[24] that cleavage of tertiary amines with phenyl chloroformate and alkali is very facile, application of this reaction to XVI yielded the corresponding methyl-N-phenylcarboxynaphthylamine (XVIII) which has so far resisted attempts at hydrolysis. The reactions of tetrafluorobenzyne described above indicate its high reactivity towards aromatic species which is being exploited in work now in progress.

EXPERIMENTAL

Reaction of tetrafluorobenzyne with benzene

(a) *In benzene/hexane.* n-Bu-Li (8·3 g) in n-hexane (55 ml) was added dropwise to a stirred soln of pentafluorobenzene (20·7 g) in benzene (200 ml) at 0°. The reaction mixture was stirred 5 hr at 15°, washed with 4N H_2SO_4 (50 ml) and water (50 ml), the organic layer was separated, dried ($MgSO_4$) and the solvents evaporated to yield 2,3-*(tetrafluorobenzo)bicyclo*[2,2,2]*octatriene* (I; 8·5 g) m.p. 70–72° from light petroleum. (Found: C, 63·7; H, 2·6; F, 34·1. M.W. 226 (mass spectrum) $C_{12}H_4F_4$ requires: C, 63·7; H, 2·7; F, 33·6% M.W. 226).

(b) *In ether/hexane.* Pentafluorophenyl lithium, prepared as above from pentafluorobenzene (1·68 g) and n-BuLi in ether/hexane (4:1 20 ml), and dry benzene (5 g) in ether (10 ml) were stirred at 15° for 2 hr. Working up as before afforded a green-brown oil. (1 g). Chromatography on silica gel using carbontetrachloride followed by ether as eluants afforded 2*H*-Nonafluorobiphenyl (0·2 g) m.p. 69° identical with an authentic sample[3] and a crystalline solid (0·4 g) m.p. 80–82°. (Found: C, 49·2; H, 0·4; F, 46·1% M.W. 760). The ^{19}F NMR spectrum was complex showing three groups of peaks in the ratio 15:5:1. The ^{1}H NMR shows a complex peak. The nearest fit to the data available is a eicosafluoroquinquephenyl.

Reaction of tetrafluorobenzyne with toluene

n-BuLi (2·8 g) in hexane (20 ml) was added dropwise to pentafluorobenzene (5·3 g) in toluene (30 ml) at 0°. The reaction mixture was stirred at 0° for 3 hr and then at 15° for 12 hr, then poured into 4N H_2SO_4 (50 ml). The organic layer was separated washed with water and dried ($MgSO_4$). The solvents were distilled off at atm press to leave a viscous oil, distillation of which *in vacuo* afforded tetrafluorobenzomethylbicyclo[2,2,2]octatrienes (1·0 g) b.p. 75–80° 0·2 mm. The mixture was separated by preparative scale gas chromatography (P.E.G.A./Keiselguhr 1:5 32′ × 3/8″ column 150° 60 ml N_2/min) to yield III (87%) m.p. 39–40°. (Found: C, 65·2; H, 3·5. $C_{13}H_8F_4$ requires: C, 65·0; H, 3·3%) and II (13%) b.p. 80°/0·2 mm. (Found: C, 65·7; H, 3·3. $C_{13}H_8F_4$ requires: C, 65·0; H, 3·39%).

Reaction of tetrafluorobenzyne with o-*xylene*

n-BuLi (2·8 g) in hexane (20 ml) was added dropwise to a stirred soln of pentafluorobenzene (5·8 g) in *o*-xylene (30 ml) at 0°. After being stirred at 0° for 3 hr and then at 15° for 12 hr the mixture was poured into 4N H_2SO_4 (50 ml). Working up as described above afforded a mixture of the adducts (2·2 g, 27·6% b.p. 92–100° 0·2 mm). Separation by preparative gas chromatography afforded 2,3-*dimethyl*-5,6-*(tetrafluorobenzo)bicyclo*[2.2.2]*octatriene* (IV) m.p. 69–71°. (Found: C, 66·0; H, 3·8. $C_{14}F_4H_{10}$ requires: C, 66·2; H, 3·9%) and 1,2-*dimethyl*-5,6-*(tetrafluorobenzo)bicyclo*[2.2.2]*octatriene* (V) b.p. 90%/0·2 mm. (Found: C, 66·4; H, 3·7. $C_{14}H_{10}F_4$ requires: C, 66·2; H, 3·9%). The ratio of isomers by weight recovery was 61:39.

Reaction of tetrafluorobenzyne with m-*xylene*

In a similar experiment to that described for *o*-xylene but using *m*-xylene a mixture of the adducts (1·9 g, 25% b.p. 47–48° 0·1 mm) was obtained. Separation as before by preparative gas chromatography afforded 2,7-*dimethyl 5 tetrafluorobenzobicyclo*[2.2.2]*octatriene* (VI) m.p. 54–56°. (Found: C, 65·9; H, 4·0. $C_{14}H_{10}F_4$ requires: C, 66·2; H, 3·9%) and 1,5-*dimethyl*-2,3-*tetrafluorobenzobicyclo*[2.2.2]*octatriene* (VII) b.p. 47 0·1 mm. (Found: C, 66·3; H, 3·8. $C_{14}H_{10}F_4$ requires: C, 66·2; H, 3·9%). The isomers were in the ratio of 64:36 by weight and ^{1}H NMR integration.

Reaction of tetrafluorobenzyne with p-*xylene*

n-BuLi (2·1 g) in hexane (14 ml) was added dropwise to a soln of pentafluorobenzene (5 g) in *p*-xylene (50 ml) at 0°. The mixture was stirred at 0° for 9 hr. Working up as before afforded a single isomer (2·3 g), purification by distillation *in vacuo* and recrystallization from EtOH gave 2,5-*dimethyl*-7,8-*tetrafluorobenzobicyclo*[2.2.2]*octatriene* (VIII) m.p. 69–70° b.p. 111°/0·4 mm. (Found: C, 66·3; H, 4·0. $C_{14}H_{10}F_4$ requires: C, 66·2; H, 3·9%). No other isomer could be detected.

1,2,3,4-*Tetrafluoro*-9,10-*dihydrophenanthrene*

Pentafluorophenyl magnesium bromide (From C_6F_5Br 25 g) was prepared, in ether (30 ml), Styrene (30 ml) and cyclohexane (70 ml) were added and the solvent fractionally distilled until the reflux temp reached 81° when the residue was refluxed for 12 hr. The resulting soln was diluted with ether and poured into water (100 ml) and the ether layer separated, washed with 4N H_2SO_4 (100 ml) and dried ($MgSO_4$).

The solvent was distilled off to leave a brown residue (37·2 g). Separation of this latter in three aliquots on a silica gel column using petroleum ether (b.p. 40–60) afforded 1,2,3,4-*tetrafluoro-9,10-dihydrophenanthrene* (X; 4·1 g) m.p. 87–88·5 from EtOH. (Found: C, 66·2; H, 3·4; M.W. 252. $C_{14}H_8F_4$ requires: C, 66·6; H, 3·2% M.W. 252). 'H NMR peaks at 2·15, 2·8, 7·24 γ ratio 1:3:4. and 1,2,3,4-*tetrafluoro-9-β phenylethyl-9,10-dihydrophenanthrene* (XI) (7·3 g) as a viscous gum. (Found: C, 73·7; H, 4·7; M.W. 356. $C_{22}H_{16}F_4$ requires: C, 74·2; H, 4·5% M.W. 356). H NMR peaks at 2·1, 2·9, 7·3, 8·8 γ integral ratio 1:8:4:3.

In a similar experiment but using pentafluorophenyl lithium the same compounds together with polystyrene were obtained.

1,2,3,4-*Tetrafluorophenanthrene*

1,2,3,4-Tetrafluoro-9,10-dihydrophenanthrene (1·4 g) and Pd-C (10%, 1 g) were heated together in a sealed tube at 250° for 40 hr. Soxhlet extraction, using ether as solvent, of the tube contents yielding 1,2,3,4-*tetrafluorophenanthrene* (XII; 0·9 g) m.p. 163–164. (Found: C, 67·9; H, 2·4; F, 30·4; M.W. 250. $C_{14}H_6F_4$ requires: C, 67·2; H, 2·4; F, 30·4% M.W. 250).

In a similar experiment 1,2,3,4-tetrafluoro-9-β phenylethyl-9,10-dihydrophenanthrene (0·5 g) yielded styrene (0·1 g) and 1,2,3,4-tetrafluorophenanthrene (0·2 g) identified by their IR spectra.

2,3-*Tetrafluorobenzobicyclo*[2.2.1]*heptadiene*

Pentafluorophenylmagnesium bromide (from C_6F_5Br 7·3 g) in dry ether (20 ml) and cyclopentadiene (16 g) were heated together in a sealed tube under a N_2 atm at 100° for 12 hr. The product was washed with 4N H_2SO_4 (2 × 40 ml), water (3 × 20 ml) and dried ($MgSO_4$), distillation of the solvent afforded an oil which on fractional distillation *in vacuo* afforded dicyclopentadiene and 2,3-*tetrafluorobenzobicyclo*-[2.2.1]*heptadiene* (XIII) (1·9 g) 30% yield m.p. 43·5–44. (Found: C, 61·8; H, 2·7. $C_{11}H_6F_4$ requires: C, 61·7; H, 2·8%).

Reaction of tetrafluorobenzyne with durene

Pentafluorophenyl lithium (from C_6F_5Br, 2·5 g) in ether/n-heptane (5:1 25 ml) was maintained at −78° for 15 min. Durene (5 g) in ether (20 ml) was added and the mixture warmed to 15° and left at this temp for 2 days. After working up as before a solid (5 g) which showed two major components by GLC analysis. Separation by fractional sublimation afforded durene (3·2 g) and 2,3,5,6-*tetramethyl-7,8-benzobicyclo*[2.2.2]*octatriene* (1·5 g) m.p. 150–151 (IX). (Found: C, 68·5; H, 4·6; M.W. 282. $C_{16}H_{14}F_4$ requires: C, 68·1; H, 4·9% M.W. 282).

Reaction of tetrafluorobenzyne with thiophen

Pentafluorophenyl lithium (from C_6F_5Br 10 g) prepared as described above was stirred at −70° for 15 min, thiophen (6·8 g) was added, the soln warmed to 15° and stirred overnight. The reaction mixture was washed with 4N H_2SO_4 (50 ml) and water (2 × 50 ml), the ether layer was dried ($MgSO_4$) and the solvent evaporated to yield is viscous oil (11 g) from which 1,2,3,4-tetrafluoronaphthalene (1·5 g) precipitated. Separation of the mother liquors on a silica gel column yield the tetrafluoronaphthalene (0·6 g) and bromopentafluorobenzene (2·5 g).

In a similar experiment but separating the products by alumina chromatography pentafluorothiophenol (0·6 g) identical with an authentic sample[25] was isolated.

Tetrafluorobenzyne and tetrachlorothiophen

Pentafluorophenylmagnesium bromide (from C_6F_5Br 5 g) in ether 20 ml and tetrachlorothiophen (9 g) in cyclohexane (20 ml) and ether (20 ml) were heated under a Vigreaux column until all the ether had distilled off. Reflux for 15 hr followed by working up in the usual way afforded an oil (9·3 g) from which was isolated tetrachlorothiophen (6·3 g) and an oil 2·5 g. From a portion of the oil 0·5 g was obtained by chromatography on silica gel using petroleum ether (40-60) as eluent, 1,2,3,4-*tetrachlorofluoronaphthalene* XV (0·11 g) m.p. 147°. (Found: C, 35·4 M.W. 336–344. $C_{10}Cl_4F_4$ requires: C, 35·5% M.W. 336–344).

Pyrolysis of *tetrafluorobenzobicyclo*[2.2.2]*octatriene*. The octatriene (0·5 g) was heated at 280° for 40 hr in a sealed tube. The contents of the tube, a gas shown by IR spectroscopy to be acetylene and a solid (0·2 g) shown by IR spectroscopy and mixed m.p. to be 1,2,3,4-tetrafluoronaphthalene.

Pyrolysis of 1-*methyl-2,3-tetrafluorobenzobicyclo*[2.2.2]*octatriene*. The triene (0·1 g) was heated at 280° in a sealed tube for 40 hr to yield 1,2,3,4-tetrafluoro-5-methylnaphthalene (0·05 g) identical with a sample prepared previously[18]

Pyrolysis of 2,3-*tetrafluorobenzobicyclo*[2.2.1]*heptadiene*. The heptadiene (0·3 g) was heated at 280° for 40 hr in a sealed tube to yield 1,2,3,4-tetrafluoronaphthalene (0·2 g) identical with an authentic sample.

1,2,3,4-*Tetrafluoro*-5,8-*dihydro*-5,8-N-*methylaminonaphthalene*

Pentafluorophenyl lithium (from C_6F_5H 25 g) in ether/hexane 1:1 (100 ml) was stirred at −70° for 15 min when 1-methylpyrrole (27·5 g) was added, the soln was warmed to 15° and stirred overnight. The soln was washed with 4N H_2SO_4 (3 × 100 ml) and the viscous acid washings basified with 4N NaOH. The ppt was filtered off and washed several times with water, sublimation of the residue *in vacuo* gave 1,2,3,4-*tetrafluoro*-5,8-*dihydro*-5,8-N-*methyliminonaphthalene* (XVI; 18·2 g) m.p. 75–76°. (Found: C, 57·7; H, 3·2; M.W. 229. $C_{11}H_7F_4N$ requires: C, 57·5; H, 3·1% M.W. 229).

Vacuum distillation of the neutral extracts yielded 1-methylpyrrole and 2*H*-nonafluorobiphenyl (3·0 g).

Reactions of 1,2,3,4-*tetrafluoro*-5,8-*dihydro*-5,8(N-*methylimino*) *naphthalene*

With aqueous acid. The resublimed adduct (1·05 g) was heated in refluxing 4N HCl (25 ml) and after 4 hr the brown acid soln was extracted with ether (100 ml) and the extracts dried ($MgSO_4$). Evaporation of the extracts and sublimation of the residue under vacuum at 100° yielded a white crystalline solid, identified as N-*methyl*-5,6,7,8-*tetrafluoro*-α-*naphthylamine* XVII (0·10 g, 9·5%, m.p. 124–125° dec) by IR and UV spectroscopy. (Found: C, 57·9; H, 2·8; M.W. 229. $C_{11}H_7F_4N$ requires: C, 57·6; H, 3·1%; M.W. 229). Basification of the acid soluble extracts with a saturated soln of Na_2CO_3, and extraction of the ppt with ether, yielded starting material (0·61 g) identified by its IR spectrum.

With ethanolic acid. The adduct (0·55 g) was heated in a refluxing mixture of EtOH (40 ml) and conc HCl (7 ml) for 18 hr. The clear soln was poured into water (50 ml) and extracted as before to yield N-methyl-5,6,7,8-tetrafluoro-α-naphthylamine (0·12 g) and starting material (0·27 g) both identified by comparing their IR spectra with those of authentic samples.

With phenylchloroformate. Resublimed adduct (1·89 g) in dry CH_2Cl_2 (20 ml) was mixed with phenylchloroformate (1·5 g) at 0° and stirred for 1 hr. After stirring at room temp overnight the purple soln was poured into 4N HCl and extracted with CH_2Cl_2. The dried ($MgSO_2$) extracts were evaporated under reduced press to yield a straw-coloured oil (2·8 g) which crystallized on standing. The crystalline product was washed with hot pet. ether (b.p. 40–60°) to yield a solid (2·63 g, m.p. 76–77·5° decomposing and effervescing) which rapidly decomposed on standing to a purple oil. (Found: C, 57·2; H, 2·7%). A sample of this oil (2·3 g) was boiled with 10% NaOHaq for 30 min and the resulting yellow oil extracted with ether (3 × 50 ml). The extracts were separated, washed with 4N HCl (3 × 20 ml) and water (50 ml), dried ($MgSO_4$) and evaporated to give a yellow oil which crystallized on standing. Recrystallization from EtOH gave N-*carboxyphenyl*-N-*methyl*-5,6,7,8-*tetrafluoro*-α-*naphthylamine* XVIII (1·5 g, m.p. 90–91°). (Found: C, 62·0; H, 3·2; M.W. 349. $C_{18}H_{11}F_4NO_2$ requires: C, 61·9; H, 3·1% M.W. 349).

NMR spectroscopy

The proton NMR spectra of the adducts described previous have been analysed either by first order analysis where possible or by standard methods of second order analysis. Some spectra where a bridgehead H atom is present show coupling of surprising magnitude of the F atoms. In all cases where complex analysis was required the coupling constants obtained showed the same relative sign. The results obtained for 'H NMR are shown in Table 2.

^{19}F NMR spectra of all the compounds were very similar being of a standard AA'XX' pattern and most could be analysed by applying standard methods to one half usually the upfield half, of the spectrum. As coupling constants are so similar the results for the benzene adduct only are given in Table 3.

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