Aryne Chemistry. Part XXXIII.[1] Reactions of Tetrahalogenobenzynes with Methoxyarenes and the Photolysis and Thermolysis of Some of the Products

By P. Christopher Buxton, Neil J. Hales, Barry Hankinson, Harry Heaney,* Steven V. Ley, and Ram Prakash Sharma, Department of Chemistry, The University of Technology, Loughborough, Leicestershire LE11 3TU

The reactions of tetrahalogenobenzynes with methoxyarenes afford good yields of both 1.4-dihydro-1-methoxy-1.4-ethenonaphthalene derivatives and, in certain cases, 3,4-dihydro-1,4-ethenonaphthalen-2(1H)-ones. Thermolysis or photolysis of these compounds leads to naphthalene derivatives in high yield.

WE and others, had noted previously that the reactions of tetrahalogenobenzynes with anisole resulted in $(2 + 4)\pi$ cycloaddition in which there was a marked preference in favour of the formation of the cycloadduct bearing the methoxy-group at a bridgehead position.[2] In similar reactions with alkylbenzenes the favoured orientation was the reverse, so that with p-xylene or durene only one product was isolated.[2] We therefore decided to study reactions of tetrahalogenobenzynes with di- and poly-substituted anisoles. We also hoped that reactions with suitable methoxyarenes would lead to bis-enol ethers which would yield interesting non-enolisable β-diketones. In addition, we wished to prepare certain derivatives of 3,4-dihydro-1,4-ethenonaphthalen-2(1H)-one (benzobarrelenone) in order to obtain 1,4-dihydro-1,4-etheno-naphthalene (benzobarrelene) derivatives bearing an electron-withdrawing substituent on a double bond, thus enabling us to test our hypothesis [2c] that such compounds would readily disproportionate to naphthalene derivatives. We also expected the products of the reactions to prove useful in connection with other studies, including photochemical and thermal reactions [3] and acid-catalysed rearrangement reactions.[4]

The now well established [5] methods of generating tetrahalogenobenzynes were used and require little comment. The best yields of the cycloadducts were frequently obtained from reactions in which organometallic precursors were used for the arynes. Unlike other

workers,[2d] we found that the presence of ethylene oxide did not affect the ratio of the products in the reaction of tetrafluorobenzyne with anisole. Not surprisingly the overall yield of the adducts was lower, since some of the pentafluorophenyl-lithium is consumed by the ethylene oxide. We obtained large amounts of highly coloured impurities in many reactions in which we generated tetrachlorobenzyne either by the aprotic diazotisation of tetrachloroanthranilic acid or by the decomposition of 2-carboxytetrachlorobenzenediazonium salts. This suggested that the increased electrophilicity of these diazonium salts as compared with benzenediazonium salts could lead to the ready formation of azo-compounds with methoxyarenes.[6] In fact when 2-carboxytetrachloro-benzenediazonium chloride was decomposed in the presence of 2,3-dimethylanisole in carbon tetrachloride we obtained 3,4,5,6-tetrachloro-4'-methoxy-2',3'-di-methylazobenzene-2-carboxylic acid (1) in 35% yield in addition to the tetrachloro-1-methoxy-2,3-dimethyl-benzobarrelene (2), which was isolated in 7% yield. A similar result was obtained in a reaction of 2-carboxy-tetrachlorobenzenediazonium chloride with m-dimeth-oxybenzene in carbon tetrachloride solution. From a reaction at room temperature the azobenzene derivative (3) was isolated in 97% yield, whereas a reaction at 80° gave the ketone (4), isolated in only 12% yield. On the other hand compound (2) was obtained in 50% yield when pentachlorophenyl-lithium decomposed in the presence of 2,3-dimethylanisole.

The structures of the various products (Table 1) were

[1] Part XXXII, B. Hankinson, H. Heaney, A. P. Price, and R. P. Sharma, *J.C.S. Perkin I*, 1973, 2569.

[2] (a) J. P. N. Brewer, I. F. Eckhard, H. Heaney, and B. A. Marples, *J. Chem. Soc. (C)*, 1968, 664; (b) H. Heaney and J. M. Jablonski, *ibid.*, p. 1895; (c) H. Heaney, K. G. Mason, and J. M. Sketchley, *ibid.*, 1971, 567; (d) N. N. Vorozhtsov, N. G. Ivanova, and V. A. Barkhash, *Izvest. Akad. Nauk., S.S.S.R.*, 1967, 7, 1514.

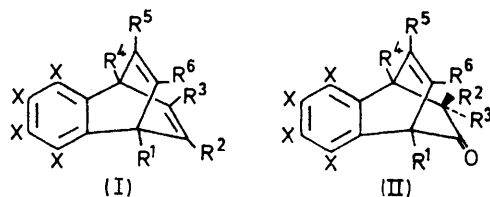[3] B. Hankinson and H. Heaney, *Tetrahedron Letters*, 1970, 1335.

[4] H. Heaney and S. V. Ley, *Chem. Comm.*, 1971, 224, 1342.

[5] H. Heaney, *Fortschr. Chem. Forsch.*, 1970, 16 (1), 35.

[6] H. Zollinger, 'Azo and Diazo Chemistry, Aliphatic and Aromatic Compounds,' Interscience, New York, 1961, p. 211.

TABLE 1

Reactions of tetrahalogenobenzynes with substituted anisoles

Aryne precursor [a]	Anisole substituents [b]	No.	Type	R^1	R^2	R^3	R^4	R^5	R^6	X	Yield (%)
E	2,3-Dimethyl-	(1)									35
		(2)	(I)	OMe	Me	Me	H	H	H	Cl	7
F	2,3-Dimethyl-	(2)									8 [c]
D	2,3-Dimethyl-	(2)									50·5
E [d]	3-Methoxy-	(3)									97
E [e]	3-Methoxy-	(4)	(II)	H	H	H	OMe	H	H	Cl	12
H	3-Methoxy-	(4)									35 [f]
B	2-Methoxy-	(5)	(II)	OMe	H	H	H	H	H	F	44
B	3-Methoxy-	(6)	(II)	H	H	H	OMe	H	H	F	61·5
D	3-Methoxy-	(6)									20·5
B	4-Methoxy-	(7)									31
		(8)	(I)	OMe	H	H	OMe	H	H	F	18
		(10)									8
B	3-Methoxy-2-methyl- [g]	(11)	(I)	OMe	Me	OMe	H	H	H	F	52
B	3-Methoxy-2-methyl- [h]	(12)									12
		(18)	(II)	H	H +	Me	OMe	H	H	F	62
B	3,5-Dimethoxy-	(13)									38
		(14)									—
B	Tetrafluorobenzo[2,3]- [j]	(16)									40
B		(19) [2a]	(I)	OMe	H	H	H	H	H	F	49
		(20) [2a]	(II)	H	H	H	H	H	H	F	10
B	k	(19)	(I)								24
		(20)	(II)								5·5
C		(19)									41
		(20)									5·5
B	α-Methyl [l]	(21)	(I)	OEt	H	H	H	H	H	F	39
		(20)									6·3
D	2-Methoxy-	(22)	(II)	OMe	H	H	H	H	H	Cl	26
G	2-Methoxy-	(22)									22
E	2-Methyl-	(23)	(I)	OMe	Me	H	H	H	H	Cl	33
F	2-Methyl-	(23)									51
E	3-Methyl-	(24)	(I)	OMe	H	Me	H	H	H	Cl	70
B	4-Methyl-	(25)	(II)	H	H	H	H	Me	H	F	45
		(26)	(I)	OMe	H	H	Me	H	H	F	21
E	4-Methyl-	(27)	(II)	H	H	H	H	Me	H	Cl	57
		(28)	(I)	OMe	H	H	Me	H	H	Cl	3·5
E	2-Bromo-	(29)	(I)	OMe	Br	H	H	H	H	Cl	28
A	2,5-Dimethyl-	(30)	(I)	OMe	Me	H	H	Me	H	F	62
E	2,5-Dimethyl-	(31)	(I)	OMe	Me	H	H	Me	H	Cl	53
F	2,5-Dimethyl-	(31)									58
A	2,6-Dimethyl-	(32)	(I)	OMe	Me	H	H	H	Me	F	43
		(33)	(II)	Me	H	Me	H	H	H	F	14
		(34)	(II)	Me	Me	H	H	H	H	F	9
D	2,6-Dimethyl-	(35)	(I)	OMe	Me	H	H	H	Me	Cl	36·5
		(36)	(II)	Me	H	Me	H	H	H	Cl	33
E	2,6-Dimethyl-	(36)									12
		(35)									10·5
A	3,5-Dimethyl-	(37)	(I)	OMe	H	Me	H	Me	H	F	40
		(38)	(II)	H	H	H	H	Me	Me	F	22
E	2-Bromo-4-methyl-	(39)	(II)	H	H +	Br	H	Me	H	Cl	27
E	2-Bromo-3-methoxy-	(40)	(II)	H	H +	Br	OMe	H	H	Cl	42

[a] A, pentafluorophenylmagnesium bromide; B, pentafluorophenylmagnesium chloride; C, pentafluorophenyl-lithium; D, pentachlorophenyl-lithium; E, 2-carboxytetrachlorobenzenediazonium chloride; F, 2-carboxytetrachlorobenzenediazonium tetrafluoroborate; G, tetrachloroanthranilic acid–pentyl nitrite; H, 3,4,5,6-tetrachloro-2-(3,3-dimethyltriazeno)benzoic acid. [b] All substituents H unless otherwise indicated. [c] No attempt made to isolate the azo-compound (1). [d] At 20 °C, for 48 h. [e] No attempt made to isolate the azo-compound (3). [f] Based on the amount of triazene consumed (see Experimental section). [g] Base hydrolysis. [h] Base hydrolysis of reaction mixture, followed by methanolysis. [j] = 1,2,3,4-Tetrafluoro-5-methoxynaphthalene. [k] Anisole + 20% ethylene oxide. [l] = Phenetole.

established by elemental analysis (Table 7) and from spectroscopic data (Tables 2 and 3).*

The reaction of tetrafluorobenzyne with veratrole gave one major product, the benzobarrelenone (5), in 44% yield, and with *m*-dimethoxybenzene the isomer (6) was the only product and was isolated in 62% yield.

In the reaction of tetrafluorobenzyne with *p*-dimethoxybenzene three products were isolated. The major products were the diketone (7) (31%), the benzobarrelene (8) (18%), which carries two bridgehead substituents. The third product, which was isolated by repeated preparative layer chromatography, was shown by elemental analysis and mass spectrometry to have the molecular formula $C_{19}H_8F_8O_2$, and hence was derived from two molecules of tetrafluorobenzyne together with one molecule of *p*-dimethoxybenzene. The ^1H n.m.r. spectrum showed the presence of bridgehead protons, methoxy-protons, and a methylene group as the AB portion of an ABX system. The i.r. spectrum showed that the second oxygen atom was present in a carbonyl group ($v_{max.}$ 1745 cm^{-1}). The mass spectrum was characterised by a prominent peak which corresponds to loss of keten from the molecular ion. Evidently this product was derived by the addition of a second molecule of tetrafluorobenzyne to the bis-enol ether (9) which gave the diketone (7) on hydrolysis. Three possible structures may be considered, arising either by $(2 + 4)\pi$ cyclo-addition to the homo-diene,[7] or by a $(2 + 2)\pi$ cyclo-addition to one or other of the enol ether residues.[8] The first of these possibilities is unlikely in view of the ready loss of keten from the molecular ion. The chemical shift data for the methylene protons suggest that the second molecule of tetrafluorobenzyne has added from the less hindered *exo*-face of the bis-enol ether (9); hydrolysis of the remaining enol ether function would then give compound (10) as the isolated product. In the majority of our reactions the initially formed enol ethers were so unstable that we were unable to obtain any evidence for their presence in reaction mixtures. However, the crude product from the reaction of tetrafluorobenzyne with 2,6-dimethoxytoluene was more stable and i.r. and ^1H n.m.r. data provided evidence for the presence of the enol ether (11), which gave the acetal (12) on methanolysis. The ^1H n.m.r. spectrum indicated that only one of the two possible epimeric acetals was obtained; the structure (12) was assigned on the grounds that initial protonation was more likely to take place from the *exo*-face of the enol ether.

We were disappointed not to isolate 1,3-diketones from reactions with 1,3-dimethoxybenzene or 2,6-dimethoxy-

toluene. We therefore investigated the reaction of tetrafluorobenzyne with 1,3,5-trimethoxybenzene. Unchanged trimethoxybenzene was removed by steam distillation, and 5,6,7,8-tetrafluoro-3-hydroxy-1-naphthylacetic acid (13) was isolated and characterised as the corresponding *O*-methyl methyl ester (14). Evidently

(1) $R^1 = R^2 = Me, R^3 = OMe$
(3) $R^1 = R^3 = OMe, R^2 = H$

(2)

(4) X = Cl
(6) X = F

(5)

(7)

(8)

(9)

(10)

(11)

(12)
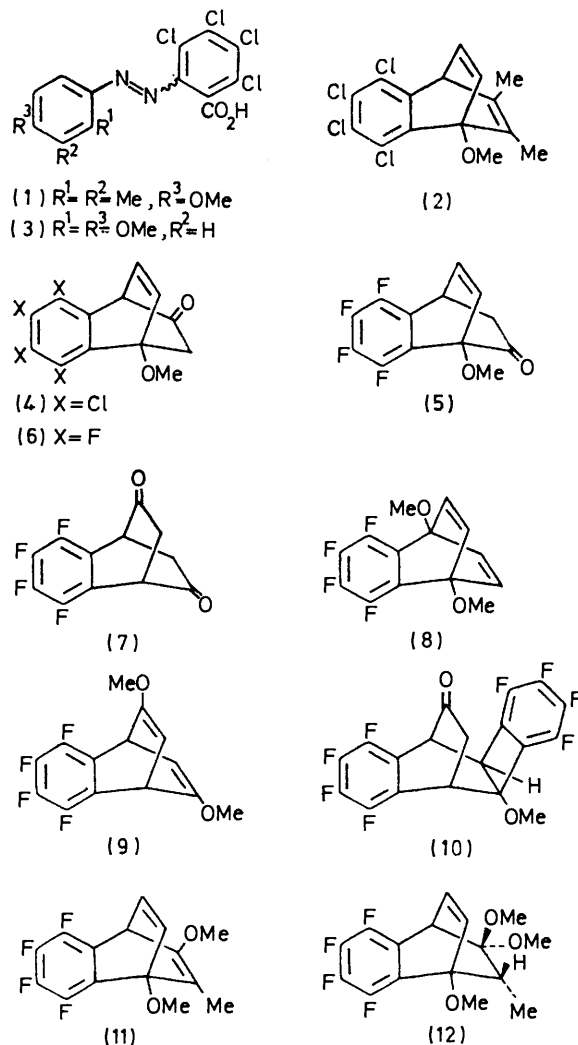
the anticipated 1,3-diketone was formed during the work-up but underwent a retro-Claisen condensation followed by elimination of methanol as shown in the Scheme. The structures of compounds (13) and (14) were established from spectral data.
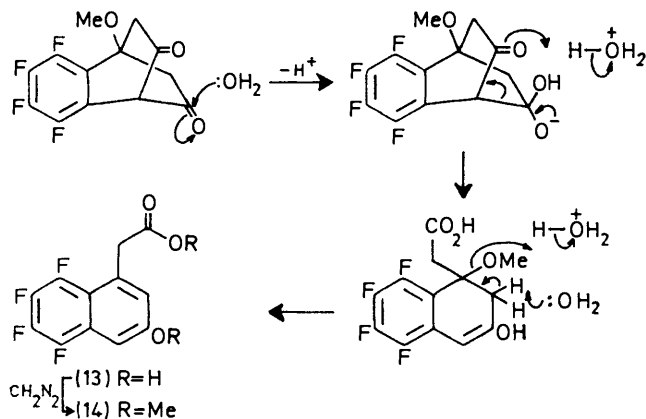
In view of our interest in thermal [1,2a] and photochemical [1,9] transformations of bridged derivatives of 1,4-dihydronaphthalene, we undertook a similar study with a number of the compounds which we had prepared. During this investigation, thermal [10] and photochemical [11] studies of similar ketones were reported.

* Tables 2 and 3 are available in Supplementary Publication No. SUP 21128 (9 pp.). For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1973, Index issue.

[7] I. N. Vorozhtsov, N. G. Ivanova, and V. A. Barkhash, *J. Org. Chem. U.S.S.R.*, 1967, **3**, 211: L. Friedman, *J. Amer. Chem. Soc.*, 1967, **89**, 3071; M. Stiles, U. Burckhardt, and G. Freund, *J. Org. Chem.*, 1967, **32**, 3718.

[8] I. Tabushi, R. Oda, and K. Okdazaki, *Tetrahedron Letters*, 1968, 3743; H. H. Wasserman, A. J. Solodar, and L. S. Keller, *ibid.*, p. 5597; L. Friedman, R. J. Osiewicz, and P. W. Rabideau, *ibid.*, p. 5735.

[9] J. P. N. Brewer, I. F. Eckhard, H. Heaney, M. G. Johnson, B. A. Marples, and T. J. Ward, *J. Chem. Soc. (C)*, 1970, 2569.

[10] A. Oku, T. Kakihana, and H. Hart, *J. Amer. Chem. Soc.*, 1967, **89**, 4554.

[11] R. K. Murray and H. Hart, *Tetrahedron Letters*, 1968, 4995; 1969, 379; J. Ipaktschi, *ibid.*, 1969, 215; R. S. Givens and W. F. Oettle, *Chem. Comm.*, 1969, 1164.

The loss of acetylenic fragments in retro-Diels–Alder reactions of benzobarrelenes have been reported previously.[2a] Thus, for example, tetrafluoro-1-methyl-benzobarrelene gave 1,2,3,4-tetrafluoro-5-methylnaphthalene in good yield. The long-range $^{19}F,^{1}H$ spin–spin coupling observed between the methyl group and the 4-fluorine atom was a particularly useful aid to proof of structure. The pyrolysis of tetrafluoro-1-methoxy-benzobarrelene *in vacuo* at 300° gave 1,2,3,4-tetrafluoro-5-methoxynaphthalene (15) in 92% yield. The ^{1}H n.m.r. spectrum of this compound showed no evidence for long-range $^{19}F,^{1}H$ coupling involving the methoxy-group.
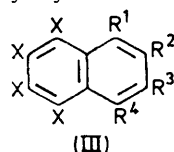
n.m.r. spectrum of which the methoxy-signal appeared as a triplet ($|J|$ 1·9 Hz). The precise reasons for the lack of long-range coupling in compound (15) are obscure, but

(15)

(16)

(17)
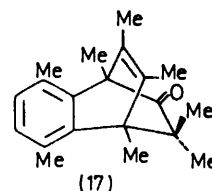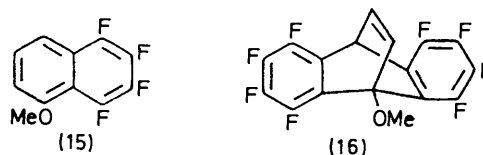
this result suggests that the passage of information concerning spin–spin interactions occurs through the bonds in completely aromatic systems.

The fact that the mass spectra of a number of the benzobarrelenones which we have prepared did not show molecular ion peaks, but did show high intensity peaks corresponding to the loss of keten, encouraged us to undertake pyrolytic and photolytic studies on these compounds. The thermal ejection of dimethylketen from the benzobarrelenone (17) has been reported [10] but requires temperatures of 450—500°. Using the compounds which we have prepared we found that the keten is eliminated from benzobarrelenones in high yield at much lower temperatures (*ca.* 300°). These results are

SCHEME

In order to be certain that our structural assignment was correct we prepared 1,2,3,4-tetrafluoronaphthalen-5-ol

TABLE 4

Pyrolyses of adducts

(III)

Adduct no.[a]	Temp. (°C)	No.	Type	R¹	R²	R³	R⁴	X	Yield (%)
(5)	300	(15)	(III)	OMe	H	H	H	F	79
(6)	300	(15)	(III)	OMe	H	H	H	F	94
(12)	300	(15)	(III)	OMe	H	H	H	F	87
(18)	300	(15)	(III)	OMe	H	H	H	F	98
(19)	300	(15)	(III)	OMe	H	H	H	F	92
(20)	270	(41) [2a]	(III)	H	H	H	H	F	87
(25)	360	(43) [2a]	(III)	H	Me	H	H	F	86
(21)	250	(47)	(III)	OEt	H	H	H	F	62
(26)	350	(48)	(III)	OMe	H	H	Me	F	71
(7)	400	Recovered unchanged							

[a] Numbering as in Table 1.

by acid-catalysed cleavage [12] of 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-epoxynaphthalene and by pyrolysis of the same compound. Methylation of the phenol with diazomethane then gave compound (15). We also carried out a reaction of tetrafluorobenzyne with compound (15) and obtained the octafluorodibenzobarrelene (16) in the ^{1}H

collected in Table 4. Similarly, we also obtained tetrahalogenonaphthalenes in high yields (Table 5) when we irradiated ethereal solutions of the benzobarrelenones either in quartz apparatus or through Pyrex.* These results thus complement those obtained by other workers.

* The u.v. spectra for the naphthalenes are collected in Table 6, which is available in Supplementary Publication No. SUP 21128.

[12] P. L. Coe, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1962, 3227.

TABLE 5

Photolyses of adducts in diethyl ether at 35 °C, under dry nitrogen

Adduct no.[a]	Time (h)	Concn. (mg ml⁻¹)	No.	Type	R^1	R^2	R^3	R^4	X	Yield (%)
(5)	4	2·5	(15)	(III)	OMe	H	H	H	F	97
(6)	3		(15)	(III)	OMe	H	H	H	F	88
(18)	3		(15)	(III)	OMe	H	H	H	F	81
(20)	3	1	(41) [2a]	(III)	H	H	H	H	F	98
(25)	3	0·5	(42) [2a]	(III)	H	Me	H	H	F	92
(39)	5	8	(43) [2a]	(III)	Me	H	Me	H	F	84
b	5	8	(44) [2a]	(III)	Me	H	H	H	F	94
(4)	16 [c]	10	(45)	(III)	OMe	H	H	H	Cl	42
(27)	7 [c]	1·7	(46)	(III)	H	Me	H	H	Cl	43

[a] Numbering as in Table 1. [b] 5,6,7,8-Tetrachloro-3,4-dihydro-4-methyl-1,4-ethenonaphthalen-2(1H)-one. [c] At 20 °C.

TABLE 7

Analytical and other data

Compound [a]	M.p. (°C)	Recryst. solvent [b]	Formula	% Found (Required) C	H	X	M^+
1	224—226	F	$C_{16}H_{12}Cl_4N_2O_3$	45·6 (45·5)	2·9 (2·8)	6·8 [c] (6·65)	
2	155—156	C	$C_{15}H_{12}Cl_4O$	51·4 (51·4)	3·5 (3·4)		350
3	218—221	C	$C_{15}H_{10}Cl_4N_2O_4$	42·5 (42·4)	2·3 (2·4)	6·7 [c] (6·6)	424
4	146—148	D	$C_{13}H_8Cl_4O_2$	46·4 (46·2)	2·1 (2·4)		296 [d]
5	96—97	B	$C_{13}H_8F_4O_2$	57·5 (57·35)	3·05 (2·95)	28·1 (27·9)	
6	79—81	B	$C_{13}H_8F_4O_2$	57·7 (57·35)	2·95 (2·95)	27·7 (27·9)	
7	161—164		$C_{12}H_6F_4O_2$	55·55 (55·85)	2·4 (2·35)		
8	79—81		$C_{14}H_{10}F_4O_2$	58·95 (58·75)	3·5 (3·5)		
10	176—178		$C_{19}H_8F_8O_2$	54·6 (54·3)	2·0 (1·9)		
12	138—138·5		$C_{16}H_{16}F_4O_3$	57·85 (57·85)	4·8 (4·85)		
13	Analysed as the O-methyl methyl ester [see (14)]						
14	123—124		$C_{14}H_{10}F_4O_3$	55·6 (55·6)	3·3 (3·55)		
15	76	e	$C_{11}H_6F_4O$	56·9 (57·3)	2·7 (2·6)	33·3 (33·0)	
16	128—130		$C_{17}H_6F_8O$	53·7 (54·0)	1·45 (1·6)		
18	186—188	B	$C_{14}H_{10}F_4O$	58·4 (58·75)	3·45 (3·5)		
19	80—82	A	$C_{13}H_8F_4O$	60·9 (60·9)	3·25 (3·15)	29·65 (29·65)	256
20	81—83	B	$C_{12}H_6F_4O$	59·4 (59·5)	2·35 (2·5)	31·1 (31·35)	
21	41—46	e	$C_{14}H_{10}F_4O$	62·25 (62·25)	3·65 (3·75)	28·0 (28·1)	
22	163—165	A	$C_{13}H_8Cl_4O_2$	46·4 (46·2)	3·0 (2·4)		338
23	134—136	C	$C_{14}H_{10}Cl_4O$	49·5 (50·0)	3·0 (2·95)		336
24	166—167	C	$C_{14}H_{10}Cl_4O$	50·2 (50·0)	2·97 (2·95)		336
25	76—80	B	$C_{13}H_8F_4O$	60·8 (60·9)	3·0 (3·15)		
26	60—61	B	$C_{14}H_{10}F_4O_2$	62·3 (62·25)	3·9 (3·75)		
27	172	C	$C_{13}H_8Cl_4O$	48·6 (48·45)	2·50 (2·5)		280 [d]
28	191—194	C	$C_{14}H_{10}Cl_4O$	50·1 (50·0)	3·1 (2·95)		336
29	152—153	C	$C_{13}H_7BrCl_4O$	38·5 (38·9)	1·8 (1·75)		400
30	67	C	$C_{15}H_{12}F_4O$	63·2 (63·3)	4·2 (4·2)		284
31	150—153	C	$C_{15}H_{12}Cl_4O$	51·5 (51·4)	3·5 (3·4)		350
32	(110)	f	$C_{15}H_{12}F_4O$	63·3 (63·45)	4·1 (4·25)		284
33	58—60	C	$C_{14}H_{10}F_4O$	62·05 (62·25)	3·8 (3·75)		
34	85—87	C	$C_{14}H_{10}F_4O$	62·05 (62·25)	3·95 (3·75)		
35	147—149	C	$C_{15}H_{12}Cl_4O$	51·3 (51·4)	3·6 (3·4)		350
36	139—140	C	$C_{14}H_{10}Cl_4O$	50·0 (50·0)	2·8 (2·95)		308 [d]
37	83·5	C	$C_{15}H_{12}F_4O$	63·4 (63·45)	4·3 (4·25)		284
38	62—64	B	$C_{14}H_{10}F_4O$	62·3 (62·25)	3·85 (3·75)		
39	172—175	C	$C_{13}H_7BrCl_4O$	38·8 (38·9)	1·75 (1·75)		280 [g]
40	232—234	E	$C_{13}H_7BrCl_4O_2$	37·45 (37·4)	1·65 (1·7)		296 [g]
45	134—136	C	$C_{11}H_6Cl_4O$	44·7 (44·6)	2·1 (2·05)		296
46	125—127	C	$C_{11}H_6Cl_4$	47·4 (47·15)	2·25 (2·15)		280
47	(Oil)	h	$C_{12}H_8F_4O$	59·2 (59·0)	3·45 (3·3)		
48	118—120		$C_{12}H_8F_4O$	59·0 (59·0)	3·35 (3·3)		

[a] Numbering as in Tables 1, 4, and 5. [b] A, light petroleum; B, hexane; C, ethanol; D, methanol–benzene; E, benzene; F, anisole. [c] % Nitrogen. [d] $[M - CH_2CO]^+$. [e] Purified by sublimation. [f] B.p. at 4 mmHg. [g] $[M - CHBrCO]^+$. [h] Purified by t.l.c.

We shall report the details of our studies on the acid-catalysed rearrangement reactions of 1-methoxybenzo-barrelenes in later papers.

EXPERIMENTAL

General procedures are as previously reported.[1,13]

Method A.—3,5-Dimethylanisole (0·6 mol) was added to a stirred ethereal solution of pentafluorophenylmagnesium bromide [2a] [from magnesium (0·12 g atom) and bromopenta-fluorobenzene (0·10 mol)] at 20°. The temperature was raised to 80°, the excess of ether was removed by distillation, and cyclohexane was added to maintain the volume of solvent. The mixture was stirred and heated under reflux at 80° for 3 h, allowed to cool, diluted with ether (to 300

[13] H. Heaney, J. M. Jablonski, and C. T. McCarty, *J.C.S. Perkin I*, 1972, 2903.

ml), and washed with dilute hydrochloric acid. Solvents and excess of 3,5-dimethylanisole were removed under reduced pressure and the residue was purified by column chromatography (silica gel; 5% ether–light petroleum) to yield 5,6,7,8-*tetrafluoro-1,4-dihydro-1-methoxy-3,9-dimethyl-1,4-ethenonaphthalene* (37) (40%), m.p. 83·5°, τ (CDCl$_3$) 3·40—3·60 (2H, m), 5·45—5·60 (1H, m), 6·31 (3H, d, $J_{H,F}$ 2·0 Hz), and 8·09 (6H, d, J 1·5 Hz), M^+ 284; and 5,6,7,8-*tetrafluoro-3,4-dihydro-4,10-dimethyl-1,4-ethenonaphthalen-2(1H)-one* (38) (22%), m.p. 62—64°, ν$_{max.}$ (CHCl$_3$) 1740 cm^{-1}, τ (CDCl$_3$) 3·75—3·95 (1H, m), 5·40—5·60 (1H, m), and 7·85—8·20 (8H, m).

Method B. A stirred solution of pentafluorophenyl-magnesium chloride [2a] [from magnesium (30 mg atom), chloropentafluorobenzene (20 mmol), and 1,2-dibromoethane (10 mmol)] in ether at 20° was treated with 1,3-dimethoxy-benzene (20 ml). The temperature was raised to 80°, the excess of ether was removed by distillation, and cyclo-hexane was added to maintain the volume of solvent. The mixture was stirred and heated under reflux at 80° for 5 h, allowed to cool overnight, hydrolysed with an excess of dilute hydrochloric acid, and extracted with ether. Solvent and the excess of 1,3-dimethoxybenzene were removed under reduced pressure, and the residue was recrystallised from hexane to give 5,6,7,8-*tetrafluoro-3,4-dihydro-4-methoxy-1,4-ethenonaphthalen-2(1H)-one* (6) (61·5%), m.p. 79—81°, ν$_{max.}$ 1748 cm^{-1}, τ (CDCl$_3$) 2·97—3·45 (2H, AB of ABX, J_{AB} 8·25, J_{AX} 5·15, J_{BX} 2·85 Hz), 5·24—5·42 (1H. m), 6·38 (3H, d, $J_{H,F}$ 2·4 Hz), and 7·68 (2H, s).

Method C.—A stirred solution of pentafluorophenyl-lithium [from bromopentafluorobenzene (10 mmol) and n-butyl-lithium (10 mmol; as a solution in pentane)] in ether at −70° was treated with anisole (20 ml), and al-lowed to warm to 20°. The mixture was stirred at 20° overnight, treated with an excess of dilute hydrochloric acid, and extracted with ether. Solvents and the excess of ani-sole were removed under reduced pressure and the residue was purified by column chromatography (alumina; 5% ether–light petroleum) to give 5,6,7,8-tetrafluoro-1,4-di-hydro-1-methoxy-1,4-ethenonaphthalene [2a] (19) (41%) and 5,6,7,8-tetrafluoro-3,4-dihydro-1,4-ethenonaphthalen-2(1H)-one [2a] (20) (5·5%).

Method D.—A stirred solution of pentachlorophenyl-lithium [14] [from hexachlorobenzene (50 mmol) and n-butyl-lithium (57·5 mmol; as a solution in pentane)] was treated with 2,3-dimethylanisole (50 ml) at −65°. The tempera-ture was raised to 80°, the excess of ether was removed by distillation, and the solution was heated under reflux for 2 h. The mixture was allowed to cool to room temperature, hydrolysed with dilute hydrochloric acid, and extracted with ether. Solvents and excess of 2,3-dimethylanisole were removed from the extract under reduced pressure, and the residue was purified by column chromatography (alumina; 5% ether–light petroleum) to give 5,6,7,8-*tetra-chloro-1,4-dihydro-1-methoxy-2,3-dimethyl-1,4-ethenonaph-thalene* (2) (50·5%), m.p. 155—156°, τ (CDCl$_3$) 2·92 (1H, dd, J 7·5 and 2·0 Hz), 3·16 (1H, dd, J 7·5 and 5·4 Hz), 5·05 (1H, dd, J 5·4 and 2·0 Hz), 6·29 (3H, s) and 8·23 (6H, s), M^+ 350.

Method E.—A stirred suspension of 2-carboxytetrachloro-benzenediazonium chloride [13] (7·7 mmol) in 2-bromo-1,3-dimethoxybenzene (8·3 mmol) and carbon tetrachloride (50 ml) was heated under reflux for 0·5 h. Solvent was removed under reduced pressure, and the residue was purified by column chromatography (silica gel). Elution with light petroleum gave pentachlorobenzene (0·12 g). Elution with

benzene gave (a) 2-bromo-1,3-dimethoxybenzene (2·8 mmol) and (b) 3-*bromo-5,6,7,8-tetrachloro-3,4-dihydro-4-methoxy-1,4-ethenonaphthalen-2(1H)-one* (40) (3·26 mmol, 42%), m.p. 232—234°, ν$_{max.}$ 1748 cm^{-1}, τ (CDCl$_3$; 100 MHz) 2·96—3·29 (2H, m), 4·84—4·98 (1H, dd, J 6·0 and 2·0 Hz), 5·56 (1H, s), and 6·30 (3H, s), m/e 296 (M^+ − CHBrCO).

Method F.—(a) 2-*Carboxytetrachlorobenzenediazonium tetra-fluoroborate.* A stirred solution of tetrachloroanthranilic acid (36·2 mmol) in tetrahydrofuran (50 ml) was treated with fluoroboric acid (40% aqueous solution; 20 ml, ca. 91 mmol) and stirred for 10 min. Solvent was removed under reduced pressure. A saturated solution of the residue in ether at −10° was treated with pentyl nitrite (42·7 mmol) during 15 min. The solution was stirred at 0° for 1 h. The voluminous precipitate was filtered off, washed with chilled ether, and air-dried to give 2-carboxytetrachloro-benzenediazonium tetrafluoroborate (61%).

(b) 5,6,7,8-*Tetrachloro-1,4-dihydro-1-methoxy-2,9-dimeth-yl-1,4-ethenonaphthalene* (31). A stirred suspension of 2-carboxytetrachlorobenzenediazonium tetrafluoroborate (9·09 mmol) in 2,5-dimethylanisole (4 ml) and carbon tetra-chloride (30 ml) was treated with a solution of pyridine (20 mmol) in carbon tetrachloride (5 ml) at 20° during 5 min. When evolution of gas had ceased the red mixture was filtered [alumina (50 g), eluted with light petroleum–ether (4 : 1; 300 ml)], and solvent and excess of 2,5-dimethyl-anisole were removed under reduced pressure, giving the ethenonaphthalene (31) (58%), m.p. 150—153°, τ (CDCl$_3$) 3·34 (1H, m) 3·65 (1H, dq, J 5·5 and 2·0 Hz), 5·10 (1H, dd, J 5·5 and 2·0 Hz), 6·28 (3H, s), 8·04 (3H, d, J 2·0 Hz), and 8·14 (3H, d, J 2·0 Hz), M^+ 350.

Method G.—A stirred solution of 1,2-dimethoxybenzene (25 ml) in 1,2-dichloroethane (100 ml) at 70° was treated concurrently with a solution of tetrachloroanthranilic acid (30 mmol) in tetrahydrofuran (10 ml) and 1,2-dichloroethane (25 ml) and a solution of pentyl nitrite (30 mmol) in 1,2-dichloroethane.[2c] The stirred solution was maintained at 70 °C for a further 2 h. The cold mixture was hydrolysed [dil. HCl (100 ml)] and extracted with ether (2 × 100 ml). The combined extracts were washed [NaOH (2 × 100 ml), water (2 × 100 ml)] and dried. Solvents and excess of 1,2-dimethoxybenzene were removed under reduced pressure, and the residue was purified by column chromatography (silica gel; 20% ether–light petroleum) to give 5,6,7,8-*tetra-chloro-3,4-dihydro-1-methoxy-1,4-ethenonaphthalen-2(1H)-one* (22) (22%), m.p. 163—165°, ν$_{max.}$ 1750 cm^{-1}, τ (CDCl$_3$) 3·10—3·25 (2H, m), 5·10—5·30 (1H, m), 6·25 (3H, s), and 7·55—8·08 (2H, ABq, J_{AB} 18·0 Hz), M^+, 338.

Method H.—A solution of 3,4,5,6-tetrachloro-2-(3,3-di-methyltriazeno)benzoic acid [13] (3 mmol) in 1,3-dimethoxy-benzene (7·3 mmol) and tetrachloroethylene (50 ml) was heated under reflux for 3 h, allowed to cool, and washed with aqueous sodium hydrogen carbonate (10% w/v; 50 ml)

Acidification and extraction of the aqueous phase with ether gave the unchanged triazene (0·75 mmol). The organic phase was dried, solvent was removed under reduced pressure, and the residue was purified by column chromato-graphy (silica gel). Elution with benzene gave 1,3-di-methoxybenzene (0·2 mmol). Elution with 5% ether–light petroleum gave 5,6,7,8-*tetrachloro-3,4-dihydro-4-methoxy-1,4-ethenonaphthalen-2(1H)-one* (4) (35% based on the amount of triazene consumed), m.p. 146—148°, ν$_{max.}$ 1750 cm^{-1}, τ (CDCl$_3$) 2·95—3·50 (2H, m), 4·88—5·13 (1H, m), 6·35 (3H,

14 M. D. Rausch, F. E. Tibbetts, and H. B. Gordon, *J. Organo-metallic Chem.*, 1966, **5**, 493.

s), and 7·25—7·90 (2H, AB, J_{AB} 17·7 Hz), m/e 296 ($M^{\cdot}$ — CH_2CO).

Reaction of 2-Carboxytetrachlorobenzenediazonium Chloride with 2,3-Dimethylanisole.—A stirred suspension of 2-carboxytetrachlorobenzenediazonium chloride [13] (9 mmol) in 2,3-dimethylanisole (10 ml) and carbon tetrachloride (30 ml) was heated under reflux for 1 h. Solvent and the excess of 2,3-dimethylanisole were removed under reduced pressure, and the residual dark red solid was washed with chloroform and recrystallised from anisole giving 3,4,5,6-*tetrachloro-4′-methoxy-2′,3′-dimethylazobenzene-2-carboxylic acid* (1) (8·54 mmol, 35%), m.p. 224—226°, τ [$(CD_3)_2SO$] 2·40 (1H, d, J 9·4 Hz), 3·01 (1H, d, J 9·4 Hz), 6·13 (3H, s), 7·47 (3H, s), and 7·82 (3H, s), $\lambda_{max.}$ (EtOH) (log ε) 260sh (4·08) and 364 nm (4·17). Chromatography (silica gel) of the chloroform washings gave 5,6,7,8-*tetrachloro-1,4-dihydro-1-methoxy-2,3-dimethyl-1,4-ethenonaphthalene* (2) (1·77 mmol, 7%), m.p. 155—156°, τ (CDCl$_3$) 2·92 (1H, dd, J 7·5 and 2·0 Hz), 3·16 (1H, dd, J 7·5 and 5·4 Hz), 5·05 (1H, dd, J 5·4 and 2·0 Hz), 6·92 (3H, s), and 8·23 (6H, s), M^+ 350.

Reaction of 2-Carboxytetrachlorobenzenediazonium Chloride with 1,3-Dimethoxybenzene at 20°.—A suspension of 2-carboxytetrachlorobenzenediazonium chloride [13] (34·1 mmol) in 1,3-dimethoxybenzene (43·5 mmol) and carbon tetrachloride (60 ml) was maintained at 20° for 48 h. The red crystalline precipitate was filtered off and washed with benzene to give 3,4,5,6-*tetrachloro-2′,4′-dimethoxyazobenzene-2-carboxylic acid* (3) (33·3 mmol, 97%), m.p. 218—221°, τ (CDCl$_3$) 2·25—2·45 (1H, d, J 8·9 Hz), 3·15—3·50 (2H, m), 6·03 (3H, s), and 6·10 (3H, s), $\lambda_{max.}$ (EtOH) (log ε) 209 (4·34) and 385 nm (4·11), M^+ 424.

Reaction of Tetrafluorobenzyne with 1,3,5-Trimethoxybenzene.—Tetrafluorobenzyne (generated by method B) was allowed to react with an excess of 1,3,5-trimethoxybenzene. The crude product obtained by acidic hydrolysis and extraction with ether was steam distilled to remove the excess of 1,3,5-trimethoxybenzene, and the residue was extracted with aqueous sodium hydrogen carbonate. Acidification of the aqueous extract gave a white precipitate of (5,6,7,8-tetrafluoro-3-hydroxy-1-naphthyl)acetic acid (13) (38%), $\nu_{max.}$ 3500—2600br and 1700 cm⁻¹, τ (CF$_3$·CO$_2$H), 2·45 (1H, s), 2·72 (1H, s), and 5·65 (2H, d, J_{HF} 6·0 Hz).

Compound (13) was methylated with an excess of diazomethane in ether to give the *methyl ester* (14), m.p. 123—124°, $\nu_{max.}$ 1750 cm⁻¹, τ (CCl$_4$) 2·75—2·85 (1H, m), 2·93—3·20 (1H, m), 5·94 (2H, d, $J_{H,F}$ 5·4 Hz), 6·27 (3H, s, and 6·59 (3H, s), $\lambda_{max.}$ (EtOH) (log ε) 266 (3·69), 275 (3·79), 286 (3·72), 318 (3·19), and 331 nm (3·27).

Reaction of Tetrafluorobenzyne with 1,3-Dimethoxy-2-methylbenzene.—Tetrafluorobenzyne (generated by method B) was allowed to react with an excess of 1,3-dimethoxy-2-methylbenzene. The mixture was hydrolysed (basic condi-

tions) and extracted with ether. Ether and the excess of 1,3-dimethoxy-2-methylbenzene were removed under reduced pressure to leave a residue (A), which was dissolved in methanol. The solution slowly precipitated crystals of 5,6,7,8-*tetrafluoro-3,4-dihydro-4-methoxy-3-endo-methyl-1,4-ethenonaphthalen-2(1H)-one* (18) (62%), m.p. 186—188°, $\nu_{max.}$ 1744 cm⁻¹, τ (CCl$_4$) 2·88—3·44 (2H, m), 5·15—5·37 (1H, m), 6·31 (3H, d, $J_{H,F}$ 2·5 Hz), 7·52 (1H, q, J 7·0 Hz), and 9·19 (3H, d, J 7·0 Hz). Preparative t.l.c. of the mother liquors yielded 5,6,7,8-*tetrafluoro-1,2,3,4-tetrahydro-1,3,3-trimethoxy-2-endo-methyl-1,4-ethenonaphthalene* (12) (12%), m.p. 138—138·5°, τ (CCl$_4$) 3·18—3·75 (2H, m), 5·50—5·72 (1H, m), 6·42 (3H, d, $J_{H,F}$ 2·2 Hz), 6·81 (3H, s), 6·91 (3H, s), 7·86 (1H, q, J 7·0 Hz), and 9·28 (3H, d, J 7·0 Hz).

The reaction was repeated. Preparative t.l.c. (silica gel; 50% benzene–hexane) of the residue (A) gave a single unstable product: 5,6,7,8-tetrafluoro-1,4-dihydro-1,3-dimethoxy-2-methyl-1,4-ethenonaphthalene (11) (52%), τ (CCl$_4$) 2·70—3·55 (2H, m), 5·06 (1H, m), 6·24 (3H, m), 6·42 (3H, s), and 8·30 (3H, s), $\nu_{max.}$ 2855, 1688, 1603, and 1490 cm⁻¹. Compound (11) was hydrolysed by contact with atmospheric moisture. The extent of reaction was monitored by the growth of the i.r. carbonyl peak at 1744 cm⁻¹, characteristic of (18). Compound (11) was also treated with methanol to yield a solution containing a mixture of compounds (18) and (12) (by n.m.r.).

Pyrolysis of 5,6,7,8-*Tetrafluoro-1,4-dihydro-1-methoxy-1,4-ethenonaphthalene* (19) (with J. P. N. BREWER).—The ethenonaphthalene (0·59 mmol) was heated at 300° for 12 h in an atmosphere of dry nitrogen at a pressure of 0·2 mmHg (at 20°) in a sealed 500 ml ampoule. The ampoule was allowed to cool to 20°, then opened, and the contents were extracted with ether. T.l.c. (silica gel; hexane) of the extract gave 1,2,3,4-*tetrafluoro-5-methoxynaphthalene* (15) (92%), m.p. 76°, τ (CCl$_4$) 2·38—2·76 (2H, m), 3·10—3·26 (1H, m), and 6·04 (3H, s), $\lambda_{max.}$ (EtOH) (log ε) 292 (3·77), 311 (3·66), 321sh (3·52), and 325 nm (3·59).

Photolysis of 5,6,7,8-*Tetrafluoro-3,4-dihydro-1,4-ethenonaphthalen-2(1H)-one* (20).—A solution of the ethenonaphthalene (0·21 mmol) in ether (50 ml) under dry, oxygen-free nitrogen was heated under reflux and irradiated (Hanovia medium-pressure mercury vapour lamp, quartz flask) for 3 h. Solvent was removed under reduced pressure to yield 1,2,3,4-tetrafluoronaphthalene (43) [2a] (98%).