

Aryne Chemistry. Part XXXII.¹ Reactions of Tetrahalogenobenzenes with 6,6-Dialkylfulvenes, and the Photoisomerisation and Thermal Reactions of Derived Products

By Barry Hankinson, Harry Heaney,* Anthony P. Price, and Ram Prakash Sharma, Department of Chemistry, The University of Technology, Loughborough, Leicestershire LE11 3TU

Reactions of tetrahalogenobenzenes with 6,6-dialkylfulvenes gave the expected 1,4-dihydro-1,4-methanonaphthalenes. Isomerisation of the strained double bond occurred during the catalytic hydrogenation of 5,6,7,8-tetrafluoro-1,4-dihydro-9-isopropylidene-1,4-methanonaphthalene (1). Mass spectra of compound (1) and analogues are reported. The high temperature reactions of a number of dihydro-analogues of compound (1) resulted mainly in isomerisations to derivatives of cyclopentindene, and the di- π -methane photoisomerisation of compound (1) occurred in high yield in solution in acetone.

REACTIONS of fulvenes with dienophiles² include the reaction of 6,6-dimethylfulvene with benzyne.³ Our interest in thermal⁴ and photochemical⁵ reactions of similar systems prompted the present study.⁶ Since the

¹ Part XXXI, H. Heaney, J. M. Jablonski, and C. T. McCarty, *J.C.S. Perkin I*, 1972, 2903.

² A. S. Onishchenko, 'Diene Synthesis,' Israel Program for Scientific Translations, Jerusalem, 1964; J. Sauer, *Angew. Chem. Internat. Edn.*, 1966, **5**, 211.

³ R. Muneoyuki and H. Tanida, *J. Org. Chem.*, 1966, **31**, 1988.

⁴ J. P. N. Brewer, I. F. Eckhard, H. Heaney, and B. A. Marples, *J. Chem. Soc. (C)*, 1968, 664.

majority of our work was completed a study of the photoisomerisation of 1,4-dihydro-9-isopropylidene-1,4-methanonaphthalene has been reported,⁷ and very recently accounts of the generation and reactions of

⁵ 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; and references cited therein.

⁶ Preliminary communication, H. Heaney, S. V. Ley, A. P. Price, and R. P. Sharma, *Tetrahedron Letters*, 1972, 3067.

⁷ W. Eberbach, P. Wursch, and H. Prinzbach, *Helv. Chim. Acta*, 1970, **53**, 1235.

8,8-dimethylisobenzofulvene have appeared.⁸ We therefore only report in detail the points in our study which differ from the other work.

We carried out reactions of 6,6-dimethyl- and 6,6-diethylfulvene with tetrafluorobenzene. The aryne was generated from pentafluorophenyl-lithium and from pentafluorophenylmagnesium bromide. Reactions of 6,6-dimethylfulvene with tetrachlorobenzene were also studied; the precursors for the aryne were pentachlorophenyl-lithium and tetrachloroanthranilic acid. In each of these reactions the expected derivatives of 1,4-dihydro-9-isopropylidene-1,4-methanonaphthalene [(1)–(3)] were isolated. In the reaction of 6,6-dimethylfulvene with tetrafluorobenzene in which we used a 1:1 ratio of the diene to pentafluorophenyl-lithium two additional products were isolated. These were shown to be 2-bromononafluorobiphenyl and 5-pentafluorophenyl-6,7,8-trifluoro-1,4-dihydro-9-isopropylidene-1,4-methanonaphthalene (4), derived from the reaction between 3-pentafluorophenyltrifluorobenzene and 6,6-dimethylfulvene. Products derived from this aryne have been noted previously⁹ in reactions involving pentafluorophenyl-lithium. The structure of compound (4) followed from the close similarity of its ¹H n.m.r. spectrum to that of compound (1), from the general similarity of the important fragmentations in the mass spectra of compounds (1) and (4) and their tetrahydro-derivatives (Figures 1 and 2); and from an analysis of the ¹⁹F n.m.r. spectrum of compound (4).

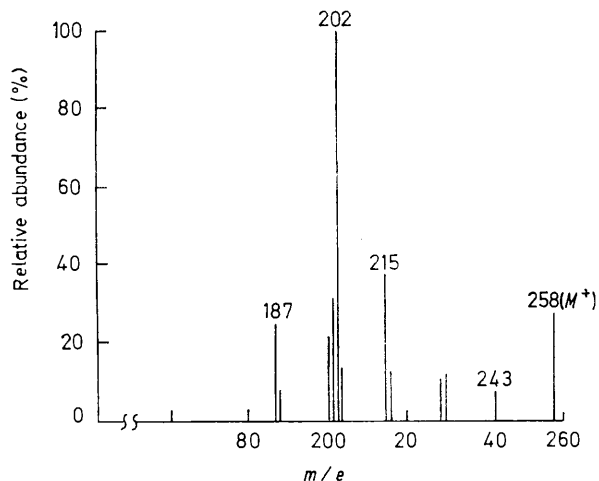


FIGURE 1 Mass spectrum of 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-isopropyl-1,4-methanonaphthalene (9)

Photoisomerisation of compound (1) proceeded efficiently in acetone solution (Hanovia 450 W medium-pressure source) and gave, as expected,^{5,7,10} tetracyclo-

⁸ H. Tanida, T. Irie, and K. Tori, *Bull. Chem. Soc. Japan*, 1972, **45**, 1999; M. N. Paddon-Row, P. L. Watson, and R. N. Warrener, *Tetrahedron Letters*, 1973, 1033.

⁹ B. Hankinson, H. Heaney, and R. P. Sharma, *J.C.S. Perkin I*, 1972, 2372; and references cited therein.

¹⁰ See for example R. S. Davidson in 'Organic Reaction Mechanisms,' ed. B. Capon and C. W. Rees, Wiley-Interscience, London, 1970, p. 544; 1971, p. 499.

undecatriene (5) in 94% yield. In contrast to the reported⁷ photoisomerisation of the unfluorinated analogue a high degree of polymerisation was observed during the photoisomerisation of compound (1) in either pentane or pentane containing 10% of acetone.

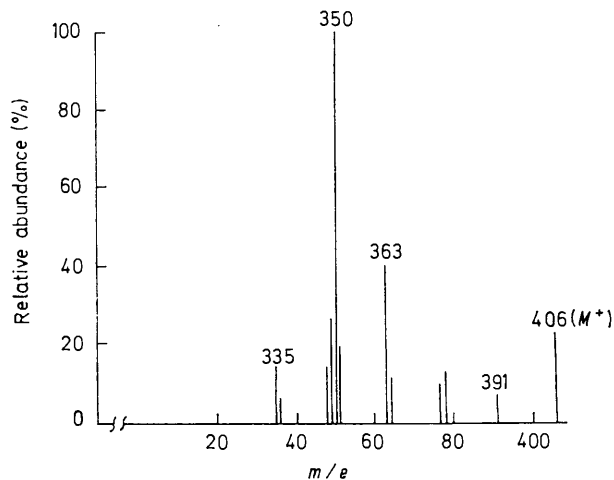


FIGURE 2 Mass spectrum of 6,7,8-trifluoro-1,2,3,4-tetrahydro-9-isopropyl-5-pentafluorophenyl-1,4-methanonaphthalene

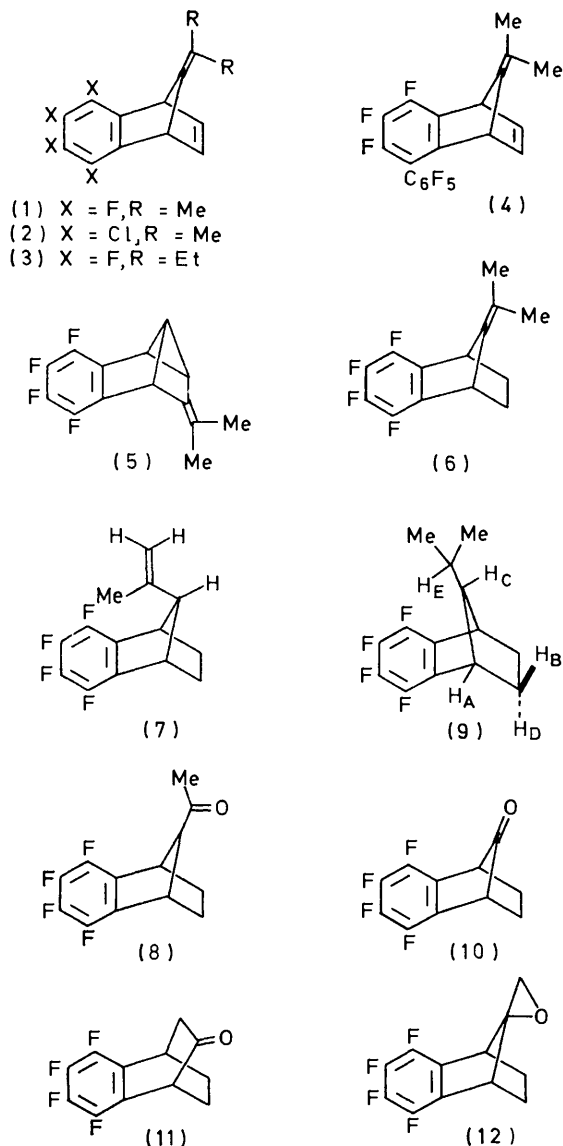
In order to study the thermal reactions of the product we hydrogenated compound (1). In spite of the presence of di- and tetra-substituted double bonds the hydrogenation proceeded without a break and led to the uptake of 2 mol. equiv. of hydrogen in the presence of palladium-carbon at room temperature. G.l.c. showed that two intermediate hydrogenation products were formed. When a small quantity of catalyst was used and the hydrogenation was carried out at 0 °C a break in the uptake of hydrogen was detected and the dihydro-derivative (6) was isolated in high yield. Hydrogenation of compound (6) produced an intermediate which eventually gave the tetrahydro-derivative. G.l.c. showed that the maximum concentration of the intermediate was present after the addition of 0.5 mol. equiv. of hydrogen to compound (6). The intermediate was isolated by preparative layer chromatography and shown, by elemental analysis and high resolution mass spectrometry, to be isomeric with the starting material. Structure (7) was suggested by the ¹H n.m.r. spectrum, in particular the expected¹¹ olefinic multiplets at τ 5.23–5.40 and 5.40–5.56, and the i.r. spectrum (ν_{max} 888s and 1780w cm^{-1}).¹² Ozonolysis of compound (7) gave 9-acetyl-5,6,7,8-tetrafluoro-1,4-dihydro-1,4-methanonaphthalene (8). The isomerisation of the double bond was studied further and it was shown that the reaction only proceeded in the presence of both the catalyst and hydrogen. Although evidence for double-bond migration has been adduced previously,¹³ the isolation of an

¹¹ See for example J. Hine and D. B. Knight, *J. Org. Chem.*, 1970, **35**, 3946.

¹² L. J. Bellamy, 'The Infra-red Spectra of Complex Molecules,' Methuen, London, 1958, p. 34.

¹³ See for example R. L. Augustine, 'Catalytic Hydrogenation,' Arnold, London, 1965; J. E. Germain, 'Catalytic Conversion of Hydrocarbons,' Academic Press, London, 1969.

isomeric olefin is not common. Presumably the driving force for the isomerisation is the release of strain associated with the bridging sp^2 -hybridised carbon atom in



compound (6). Although evidence for double-bond isomerisation was observed on hydrogenation in the presence of platinum, none was observed in the presence of Raney nickel (W4). The structure of the tetrahydro-derivative obtained by complete hydrogenation of compound (1) was not immediately obvious. It was expected that 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-isopropyl-1,4-methanonaphthalene (9) would show a doublet in the ^1H n.m.r. spectrum associated with the isopropyl group. At 60 MHz the methyl signal appeared to be a broadened singlet. This anomaly led us to carry out further chemical interconversions. Ozonolysis of compound (6) gave 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-1,4-methano-

* *Added in Proof.*—Additional double irradiation experiments carried out at 90 MHz confirm the assignment of the complex splitting patterns observed at low field.

naphthalen-9-one (10), which was converted with diazomethane¹⁴ into the known¹⁵ 5,6,7,8-tetrafluoro-1,4-ethano-2-tetralone (11) and the epoxide (12). The reason for the absence of the methine doublet in the 60 MHz ^1H n.m.r. spectrum of compound (9) was resolved when we obtained a 220 MHz spectrum (Figure 3). The methine proton (H_E) resonates at almost the same chemical shift as the methyl groups, owing to anisotropic shielding by the aryl residue. Thus even at 220 MHz the spectrum is not completely resolved and an apparent coupling constant of 5.4 Hz was observed. Irradiation at the frequency of the multiplet due to H_E caused the doublet from H_C to collapse to a singlet. The other

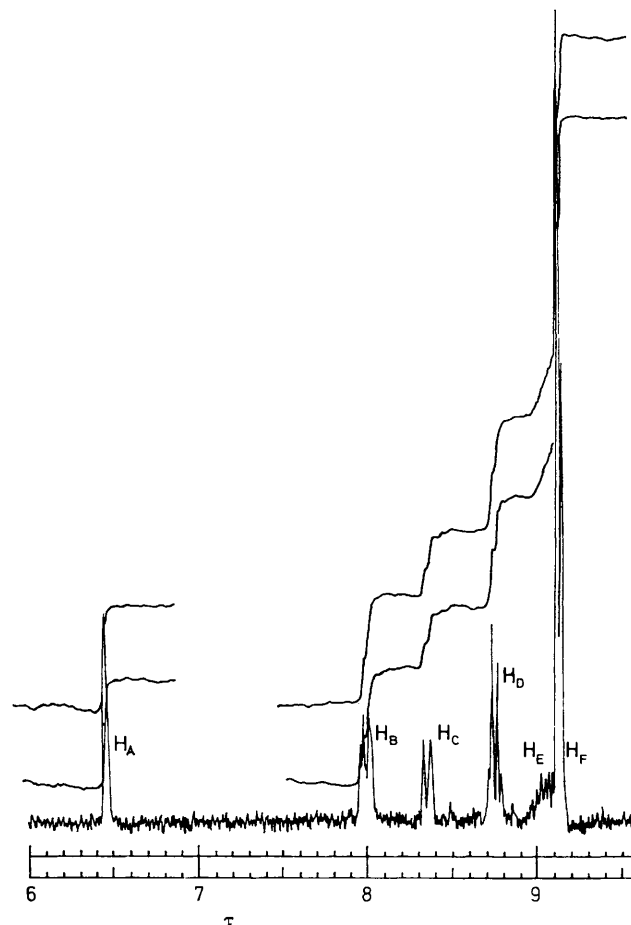


FIGURE 3 220 MHz ^1H N.m.r. spectrum of 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-isopropyl-1,4-methanonaphthalene (9)

assignments are entirely as expected,¹⁶ although certain of the splitting patterns are unexpectedly simple.*

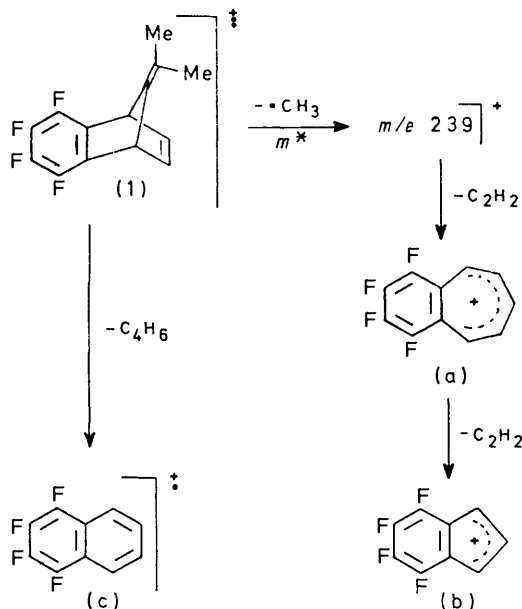
We have previously reported the mass spectral fragmentation of adducts formed between tetrafluorobenzene and simple benzene derivatives;⁴ we report here some examples of mass spectral fragmentations of compounds

¹⁴ R. S. Bly, R. K. Bly, and F. B. Culp, *J. Org. Chem.*, 1970, **35**, 2235.

¹⁵ H. Heaney and S. V. Ley, Unpublished results.

¹⁶ L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon, Oxford, 1969.

prepared in this study. The initial fragmentation of the molecular ion derived from compound (1) involves the alicyclic hydrocarbon framework and is outlined in Scheme 1. The formal loss of acetylenic fragments



SCHEME 1

TABLE 1

Mass spectral data

Compound	<i>m/e</i>	Relative abundance (%)	Ion	<i>m*</i>	Transition
(1)	254	100	<i>M</i> ⁺		
	239	70	<i>M</i> - CH ₃	224.9	254 → 239
	213	33	239 - C ₂ H ₂		
	200	63	<i>M</i> - C ₄ H ₆		
	187	33	213 - C ₂ H ₂		
(4)	402	100	<i>M</i> ⁺		
	387	53	<i>M</i> - CH ₃	372.6	402 → 387
	367	17	387 - HF	348.1	387 → 367
	361	12	367 - C ₂ H ₂		
	348	16	367 - F		
(6)	256	20	<i>M</i> ⁺		
	241	27	<i>M</i> ⁺ - CH ₃	226.9	256 → 241
	228	100	<i>M</i> ⁺ - C ₂ H ₄	203.0	256 → 228
	213	56	241 - C ₂ H ₄		
	200	41	228 - C ₂ H ₄		
	187	24	213 - C ₂ H ₂		
(13)	322	22	<i>M</i> ⁺		
	307	33	<i>M</i> - CH ₃		
	294	100	<i>M</i> - C ₂ H ₄	268.3	322 → 294
	279	20	307 - C ₂ H ₄		
	266	27	294 - C ₂ H ₄	240.7	294 → 266
	257	11	292 - Cl		
(14)	184	25	<i>M</i> ⁺		
	169	63	<i>M</i> - CH ₃		
	156	100	<i>M</i> - C ₂ H ₄	125.5	184 → 156
	141	70			
	128	43	156 - C ₂ H ₄		
	115	30	141 - C ₂ H ₂		

which result in the formation of the ions (a)—(c) (Tables 1 and 2) is similar to the fragmentation of the tetrafluorobenzene adducts of methyl-substituted benzene derivatives.⁴ The major fragmentation of compounds (6), (13), and (14) involves the loss of ethylene (Scheme 2

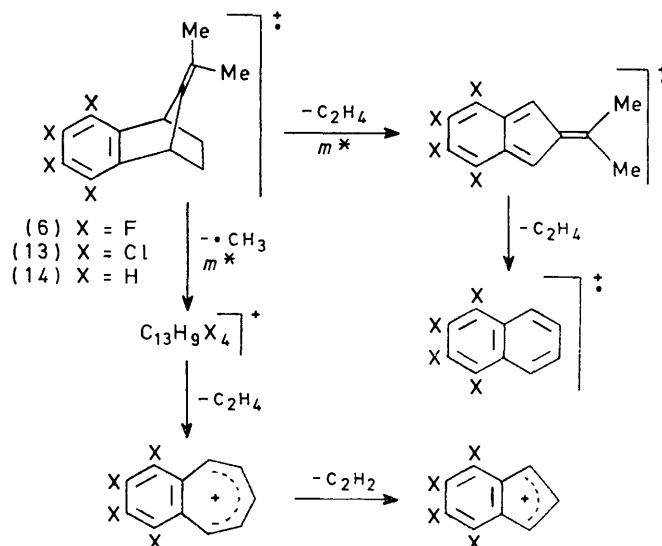
and Tables 1 and 2). The *M*⁺ - 28 ions may be formally regarded as having an isobenzofulvene structure. In the mass spectrum of compound (10) we were unable to observe the molecular ion, even at 12 eV and with the ion source at 70 °C. The base peak at *M*⁺ - 28 corresponded to the loss of carbon monoxide.

TABLE 2

Precision mass measurements

Compound	Measured mass	Formula	Calculated mass
(1)	254.0721	C ₁₄ H ₁₀ F ₄	254.0718
	200.0248	C ₁₀ H ₄ F ₄	200.0248
	187.0165	C ₉ H ₃ F ₄	187.0171
(6)	256.0878	C ₁₄ H ₁₂ F ₄	256.0876
	228.0561	C ₁₂ H ₈ F ₄	228.0562
	213.0325	C ₁₁ H ₆ F ₄	213.0327
(13)	200.0243	C ₁₀ H ₄ F ₄	200.0248
	319.9713	C ₁₄ H ₁₂ ³⁵ Cl ₄	319.9695
	291.9367	C ₁₂ H ₈ ³⁵ Cl ₄	291.9380
(14)	184.1246	C ₁₄ H ₁₆	184.1252
	156.0931	C ₁₂ H ₁₂	156.0938

In view of the mass spectral results and our interest^{4,17} in apparent similarities between mass spectral and thermal processes, we investigated the high temperature thermal reactions of compounds (6), (13), and (14). Flow pyrolysis¹⁸ of these compounds in each case gave a mixture of products (Scheme 3), in combined yield of ca. 55–75%. Chromatography of each pyrolysate gave as the major product the appropriate cyclopent[*a*]-indene derivative [(16)—(18)] together with a smaller amount of the isopropenylindene derivative [(19)—(21)]. The structures of the products were established by



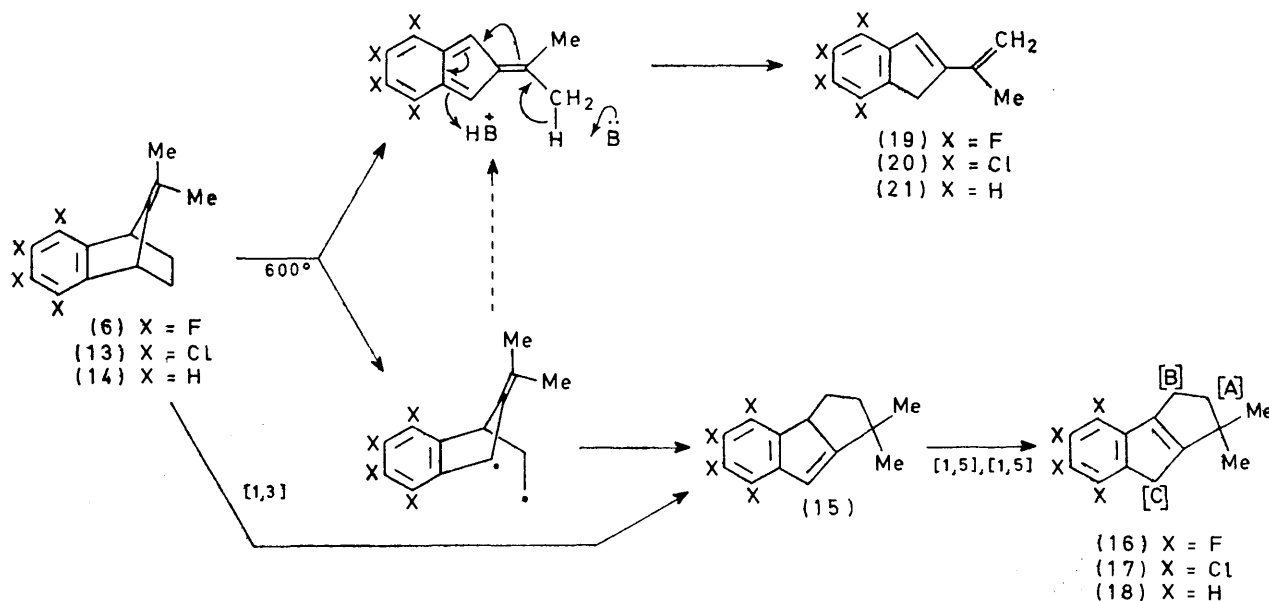
SCHEME 2

elemental analysis and by spectroscopic methods. For example the 220 MHz ¹H n.m.r. spectrum of compound (18) showed methyl signals at τ 8.8 and the methylene signals at τ 7.83 (t, *J* 7 Hz, [A]), 7.45 (m, [B]) and 6.90

¹⁷ H. Heaney and A. P. Price, *J.C.S. Perkin I*, 1972, 2911, and references cited therein.

¹⁸ J. A. Oliver and P. A. Ongley, *Chem. and Ind.*, 1965, 1024.

(t, J 2.5 Hz, [C]). Spin-spin decoupling experiments showed that the methylene group [B] was coupled to the other two methylene groups. The magnitude of the homoallylic coupling constant is in the predicted range.¹⁶ Scheme 3 shows two possible pathways to the compounds (16)—(18) which involve the intermediacy of compounds of type (15). The formation of the isolated products is not unexpected in view of the known isomerisation of indenenes by a series of [1,5] sigmatropic shifts.¹⁹ The fact that the isomerisation of the compounds (6), (13), and (14) can occur *via* intermediates of type (15) involving a thermally allowed [1,3] sigmatropic shift^{19a,20} seems to support the implied view²¹ that stepwise retro-Diels-Alder reactions occur in carbon-carbon



SCHEME 3

bridged systems which do not have alternative symmetry-allowed pathways. Compounds (1) and (9) were unchanged after experiments carried out under conditions identical with those used in the flow pyrolyses of compounds (6), (13), and (14).

The isolation of small amounts of the isopropenylindenenes (19)–(21) suggests that they are formed by retro-Diels-Alder reactions which give the respective 8,8-dimethylisobenzofulvene derivatives and which subsequently undergo either orbital-symmetry-disallowed reaction²² or base-catalysed prototropic shifts as indicated (Scheme 3). No cycloadducts were obtained when pyrolysis mixtures were condensed onto a cold (−195°C) finger coated with *N*-phenylmaleimide.

* Positive values of chemical shifts correspond to values to high field of the reference, as used in 'Fluorocarbons and Related Chemistry—Volume 1'; Specialist Periodical Reports, The Chemical Society, 1971, p. 270.

¹⁹ (a) R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 781; (b) J. A. Berson and G. B. Aspelin, *Tetrahedron*, 1964, **20**, 2697; (c) W. R. Roth, *Tetrahedron Letters*, 1964, 1009; (d) J. Almy and D. J. Cram, *J. Amer. Chem. Soc.*, 1970, **92**, 4316; (e) N. D. Epiotis, *ibid.*, 1973, **95**, 1191, 1206.

EXPERIMENTAL

I.r. spectra were determined for potassium bromide discs using a Perkin-Elmer 257 grating spectrometer. U.v. spectra were determined with a Unicam SP 8000 spectrophotometer. ¹H N.m.r. spectra (60 MHz) and ¹⁹F n.m.r. spectra (56.45 MHz) were obtained using a Perkin-Elmer R10 spectrometer (fluorotrichloromethane as internal standard*); 220 MHz ¹H n.m.r. spectra were determined at the P.C.M.U. Mass spectra were determined with an A.E.I. MS12 spectrometer and accurate mass measurements were obtained at the P.C.M.U. Molecular ion peaks quoted for chlorinated compounds refer to the most abundant ion in the molecular ion cluster.

Light petroleum refers to that fraction having b.p. 60–80°C unless otherwise stated. M.p.s were determined on a

Kofler hot-stage apparatus. T.l.c. was carried out on silica gel (Merck PF₂₅₄). Analytical g.l.c. was carried out using a Pye 104 series chromatograph (5 ft column of 20% SE 30 on firebrick; flame ionisation detector).

Reactions of Arynes with 6,6-Dialkylfulvenes.—Reaction of 6,6-dimethylfulvene with tetrafluorobenzene generated from pentafluorophenyl-lithium. Bromopentafluorobenzene (24.7 g, 0.1 mol) in ether (50 ml) was added to a stirred solution of *n*-butyl-lithium in hexane (47.2 ml, 0.11 mol) and ether (200 ml) at −70°C. After 1 h 6,6-dimethylfulvene (10.6 g, 0.1 mol) was added; the external cooling was then discontinued and the mixture was allowed to warm to room temperature. After 12 h the mixture was washed with aqueous hydrochloric acid (100 ml; 2M) and water and the organic layer was dried and evaporated to leave a pale brown oil (25.4 g). Preparative t.l.c. (light petroleum as eluant) gave three fractions.

²⁰ J. A. Berson and G. L. Nelson, *J. Amer. Chem. Soc.*, 1967, **89**, 5503; J. A. Berson, *Accounts Chem. Res.*, 1968, **1**, 152.

²¹ R. McCulloch, A. R. Rye, and D. Wege, *Tetrahedron Letters*, 1969, 5231; D. Wege, *ibid.*, 1971, 2337; D. Wege, personal communication, July 1972.

²² J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, *Accounts Chem. Res.*, 1972, **5**, 402; J. A. Berson, *ibid.*, p. 406.

Fraction 1 (R_F 0.55) gave 2-bromononafluorobiphenyl, m.p. and mixed m.p. 69—70 °C (lit.,²³ 69—71 °C) (2% based on bromopentafluorobenzene).

Fraction 2 (R_F 0.44) was incompletely resolved and after rechromatography ($\times 2$) gave two products, 5,6,7,8-tetrafluoro-1,4-dihydro-9-isopropylidene-1,4-methanonaphthalene (1) (48%), m.p. 80—82 °C (from light petroleum); τ 3.15—3.65 (2H, m), 5.18—5.40 (2H, m), and 8.66 (6H, s); δ 155.7 (2F, m) and 170.7 (2F, m) (Found: C, 66.35; H, 4.15%; M^+ , 254. $C_{14}H_{10}F_4$ requires C, 66.15; H, 3.95%; M , 254); and 6,7,8-trifluoro-1,4-dihydro-9-isopropylidene-5-pentafluorophenyl-1,4-methanonaphthalene (4) (14%), m.p. 141—143 °C (from light petroleum); τ 3.00—3.16 (2H, m), 5.16—5.34 (1H, m), 5.74—5.96 (1H, m), 8.44 (3H, s), and 8.53 (3H, s); δ (benzene) 148.8 (3F, m), 149.5 (1F, q), 162.1 (1F, t), 171.4 (2F, t), and 173.6 (1F, q) (Found: C, 59.65; H, 2.5%; M^+ , 402.0650. $C_{22}H_{10}F_8$ requires C, 59.7; H, 2.5%; M , 402.0658).

Reaction of 6,6-diethylfulvene with tetrafluorobenzene generated from pentafluorophenyl-lithium. Use of an excess of 6,6-diethylfulvene (3 mol. equiv.) gave 9-(1-ethylpropylidene)-5,6,7,8-tetrafluoro-1,4-dihydro-1,4-methanonaphthalene (3) (34%), m.p. 50—51 °C (from light petroleum); τ 2.90—3.21 (2H, m), 5.19—5.43 (2H, m), 8.05 (4H, q, J 8.5 Hz), and 9.1 (6H, t, J 8.5 Hz) (Found: C, 67.9; H, 4.9%; M^+ , 282. $C_{16}H_{14}F_4$ requires C, 68.1; H, 5.0; M , 282).

Reaction of 6,6-dimethylfulvene with tetrafluorobenzene generated from pentafluorophenylmagnesium bromide. 6,6-Dimethylfulvene (5.3 g, 0.05 mol) was added in dry cyclohexane (100 ml) to a solution of pentafluorophenylmagnesium bromide [from bromopentafluorobenzene (12.35 g, 0.05 mol)]. Ether was removed and the mixture was heated at 80 °C for 5 h, cooled, washed with aqueous hydrochloric acid (100 ml; 2M) and water, and dried. Evaporation gave a product which after preparative t.l.c. afforded compound (1) (36%), m.p. and mixed m.p. 80—82 °C, identical (i.r. spectrum) with authentic material.

*Reaction of 6,6-dimethylfulvene with tetrachlorobenzene generated from tetrachloroanthranilic acid.*²⁴ Tetrachloroanthranilic acid (5.5 g, 0.02 mol) in acetonitrile (75 ml) was added concurrently with a solution of pentyl nitrite (3 ml, 0.02 mol) in acetonitrile (75 ml) to a solution of 6,6-dimethylfulvene (2.12 g, 0.02 mol) in acetonitrile (50 ml) which was maintained at 50 °C. The usual work-up gave 5,6,7,8-tetrachloro-1,4-dihydro-9-isopropylidene-1,4-methanonaphthalene (2) (19%), m.p. 129—131 °C [from ethanol-chloroform (1:1 v/v)]; τ 2.98—3.30 (2H, m), 5.25—5.40 (2H, m), and 8.45 (6H, s) (Found: C, 52.2; H, 3.15%; M^+ , 320. $C_{14}H_{10}Cl_4$ requires C, 52.55; H, 3.15%; M , 320).

Reaction of 6,6-dimethylfulvene with tetrachlorobenzene generated from pentachlorophenyl-lithium.^{24a} This gave compound (2) (30%), m.p. and mixed m.p. 129—131 °C, identical (i.r. spectrum) with authentic material.

Preparation of 2-Bromononafluorobiphenyl and the Reaction of 3-Pentafluorophenyltrifluorobenzene with 6,6-Dimethylfulvene.—Bromopentafluorobenzene (24.7 g, 0.1 mol) in ether (20 ml) was added to a stirred solution of *n*-butyllithium in hexane (25 ml, 0.05 mol) and ether (250 ml) at —70 °C. The mixture was allowed to warm to room temperature whereupon it refluxed spontaneously. After 12 h normal work-up gave a pale yellow solid which yielded, after vacuum sublimation, 2-bromononafluorobiphenyl (9.8 g, 50%), m.p. 69—70 °C (lit.,²³ 69—71 °C).

²³ D. E. Fenton, A. J. Park, D. Shaw, and A. G. Massey, *J. Organometallic Chem.*, 1964, **2**, 437.

2-Bromononafluorobiphenyl (8.0 g, 0.02 mol) in ether (150 ml) was added to a stirred solution of *n*-butyllithium in hexane (10 ml, 0.02 mol) at —70 °C. 6,6-Dimethylfulvene (2.12 g, 0.02 mol) was then added and the mixture was allowed to warm to room temperature during 12 h. Work-up in the normal manner gave a brown solid which was shown to contain one major component by analytical g.l.c.; preparative t.l.c. gave 6,7,8-trifluoro-1,4-dihydro-9-isopropylidene-5-pentafluorophenyl-1,4-methanonaphthalene (4) (22%), m.p. and mixed m.p. 141—143 °C, identical (i.r. spectrum) with authentic material.

Photoisomerisation of Compound (1).—Compound (1) (2.54 g, 0.01 mol) dissolved in purified acetone (500 ml) was irradiated at room temperature with an unfiltered 450 W Hanovia medium-pressure mercury source. The reaction was followed by g.l.c. and terminated after 4 h. Evaporation, and distillation of the residue gave 8,9,10,11-tetrafluoro-5-isopropylidene-tetracyclo[5.4.0^{2,4}.0^{3,6}undeca-1(7),8,10-triene (5) (2.38 g, 94%), b.p. 105 °C at 1.0 mmHg; τ 5.87—6.08 (1H, m), 6.24—6.48 (1H, m), 6.84—7.10 (1H, m), 7.22—7.44 (1H, m), and 8.44 (6H, s) (Found: C, 66.0; H, 3.85%; M^+ , 254. $C_{14}H_{10}F_4$ requires C, 66.15; H, 3.95%; M , 254).

Hydrogenations.—Compound (1) (254 mg) in ethanol (60 ml) was hydrogenated at atmospheric pressure over pre-reduced palladium-carbon (10 mg, 5%) at 0 °C. The reaction was monitored by g.l.c. and terminated after the uptake of 1 mol. equiv. of hydrogen. The usual work-up gave 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (6) (92%), m.p. 97—99 °C (from light petroleum); τ 5.79—5.95 (2H, m), 7.85—8.80 (4H, m) and 8.36 (6H, s); δ 156.4 (2F, m) and 169.9 (2F, m); (Found: C, 65.75; H, 4.65%; M^+ , 256. $C_{14}H_{12}F_4$ requires C, 65.6; H, 4.7%; M , 256). Reduction of compound (2) similarly gave 5,6,7,8-tetrachloro-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (13) (90%), m.p. 154—155 °C (from methanol); τ 5.92 (2H, m), 7.82—8.2 (2H, m), 8.36 (6H, s), and 8.56—8.90 (2H, m) (Found: M^+ , 319.9713. $C_{14}H_{12}^{38}Cl_4$ requires M , 319.9695).

Reduction of compound (6) in ethanol at room temperature over pre-reduced palladium-carbon (10%) was monitored by g.l.c. and was terminated after the uptake of 0.5 mol. equiv. of hydrogen. The usual work-up followed by preparative layer chromatography gave as major product 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (7) (35%), m.p. 35—37 °C (from light petroleum); ν_{max} 3088, 3003, 2980, 1780, 1650, 1497, 1482, and 888 cm^{-1} ; τ 5.23—5.40 (1H, m), 5.40—5.56 (1H, m), 6.15—6.25 (2H, m), 7.23—7.42 (1H, m), 7.65—8.10 (2H, m), 8.39 (3H, s), and 8.50—8.90 (2H, m); δ 156.7 (2F, m) and 169.8 (2F, m) (Found: C, 65.65; H, 4.7%; M^+ , 256.0872. $C_{14}H_{12}F_4$ requires C, 65.6; H, 4.7%; M , 256.0875).

Reduction of compound (1) in ethanol at room temperature over palladium-carbon (5%) was terminated after the uptake of 2 mol. equiv. of hydrogen and gave 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (9) (88%), m.p. 58—59 °C (from light petroleum); τ 6.35—6.58 (2H, m), 7.78—9.93 (6H, m), and 9.16 (6H, s); δ 156.1 (2F, m) and 169.0 (2F, m) (Found: C, 65.1; H, 5.75%; M , 258.1030. $C_{14}H_{14}F_4$ requires C, 65.1; H, 5.5%; M , 258.1031). Reduction of compound (4) similarly gave 6,7,8-trifluoro-1,2,3,4-tetrahydro-9-isopropylidene-5-pentafluorophenyl-1,4-methanonaphthalene (74%), m.p. 96—98 °C (from

²⁴ (a) H. Heaney and J. M. Jablonski, *J. Chem. Soc. (C)*, 1968, 1895; (b) H. Heaney, K. G. Mason, and J. M. Sketchley, *ibid.*, 1971, 567.

light petroleum); τ 6.30—6.50 (1H, m), 6.90—7.15 (1H, m), 7.85—9.30 (6H, m), 9.20 (3H, s), and 9.25 (3H, s) (Found: C, 59.6; H, 3.3%; M^+ , 406.0963. $C_{20}H_{14}F_8$ requires C, 59.15; H, 3.45%; M , 406.0935).

Hydrogenations of compounds (6) and (7) similarly gave compound (9). Reduction of compound (1) was shown to give compound (9) in the presence of Adams catalyst and in the presence of Raney nickel (W4), but only in the former case was the intermediate (7) detected by g.l.c.

Ozonolyses.—*Compound* (6). Oxygen containing ozone was passed through a solution of compound (6) (256 mg) in dichloromethane (100 ml). The reaction was monitored by g.l.c. and was terminated when all the starting material had been converted into the ozonide. Nitrogen was passed through the solution to remove the excess of ozone and the ozonide was worked up using zinc and acetic acid in the usual manner to give 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-1,4-methanonaphthalen-9-one (10) (212 mg, 92%), m.p. 96—97 °C (from light petroleum); ν_{\max} . 1800 cm^{-1} ; τ 6.22—6.38 (2H, m) and 7.54—8.80 (4H, m); δ 154.6 (2F, m) and 168.1 (2F, m) (Found: C, 57.55; H, 2.85. $C_{11}H_6F_4O$ requires C, 57.4; H, 2.6%; m/e 202.0407 (M^+ — CO) ($C_{10}H_6F_4$ requires 202.0405).

Compound (7). Similarly this gave 9-acetyl-5,6,7,8-tetrafluoro-1,4-dihydro-1,4-methanonaphthalene (8) (86%), m.p. 86—89 °C (from light petroleum); ν_{\max} . 1707 cm^{-1} ; τ 5.90—6.10 (2H, m), 7.06—7.20 (1H, m), 7.65—8.00 (2H, m), 7.97 (3H, s), and 8.5—8.81 (2H, m); δ 156.4 (2F, m) and 169.4 (2F, m) (Found: C, 60.55; H, 4.0%; M^+ , 258. $C_{13}H_{10}F_4O$ requires C, 60.5; H, 3.9%; M , 258).

Reaction of Compound (10) *with Diazomethane.*—An excess of diazomethane in ether was added to a solution of compound (10) (460 mg) in ether (80 ml) and methanol (8 ml). The solution was kept at room temperature for 12 h, after which analytical g.l.c. showed the presence of two products in almost equal amounts. The usual work-up followed by preparative layer chromatography gave an upper band of 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-1,4-methanonaphthalene-9-spiro-2'-oxiran (12) (40%), m.p. 63—65 °C (from light petroleum); τ 6.68—6.87 (2H, m), 7.00 (2H, s), 7.42—7.90 (2H, m), and 8.41—8.77 (2H, m); δ 154.8 (2F, m) and 168.4 (2F, m) (Found: C, 59.4; H, 3.4%; M^+ , 244. $C_{12}H_8F_4O$ requires C, 59.0; H, 3.3%; M , 244).

The slower running band was 5,6,7,8-tetrafluoro-1,4-ethano-2-tetralone (11) (44%), m.p. 96—97 °C (from light petroleum); ν_{\max} . 1743 cm^{-1} ; τ 5.90—6.23 (2H, m) and 7.58—8.80 (6H, m); δ 155.2 (2F, m) and 169.9 (2F, m), identical with a sample prepared¹⁵ by catalytic hydrogenation of 5,6,7,8-tetrafluoro-1,4-etheno-2-tetralone (Found: C, 58.55; H, 3.2%; M^+ , spectrometry 244).

Thermal Reactions.—These were carried out by subliming the compounds slowly into the apparatus¹⁸ (*ca.* 90 cm tube) under nitrogen at *ca.* 3 mmHg pressure with the temperature maintained at *ca.* 600 °C.

Compound (14)³ (0.5 g) gave a brown oil (0.37 g) which was placed on a column of neutral alumina (200 g; activity I). Elution with light petroleum gave two fractions: (i) 1,2,3,8-tetrahydro-1,1-dimethylcyclopent[a]indene (18) (0.28 g, 54%), b.p. 110° at 0.5 mmHg; λ_{\max} (cyclohexane) 210 (log ϵ 4.22), 217 (4.15), 225 (4.00), 260 (4.10), 265 (4.06), and 270 nm (4.00) (Found: C, 90.5; H, 8.8%; M^+ , 184.1257. $C_{14}H_{16}$ requires C, 91.3; H, 8.7%; M , 184.1252); and (ii) 2-isopropenylindene (21) (0.1 g, 23%), m.p. 88—90 °C (from methanol); λ_{\max} (cyclohexane) 212 (log ϵ 4.14), 226 (4.12), 233 (4.15), 241 (4.06), 288 (4.23), 294 (4.26), and 314 nm (3.97); τ 2.5—3.0 (4H, m), 3.22 (1H, m), 4.75 (1H, m), 5.00 (1H, m), 6.42br (2H, s), and 7.93br (3H) (Found: C, 89.65; H, 6.4%; M^+ , 156.0925. $C_{12}H_{12}$ requires C, 92.3; H, 7.7%; M , 156.0939), which decomposed at room temperature.

Similarly compound (6) (0.4 g) gave an oil (0.29 g) which on chromatography gave two products: (i) 4,5,6,7-tetrafluoro-1,2,3,8-tetrahydro-1,1-dimethylcyclopent[a]indene (16) (0.21 g, 52.5%), m.p. 102—103 °C (from methanol); λ_{\max} (cyclohexane) 209 (log ϵ 4.2), 217 (4.18), 257 (4.06), 266 (4.0), 280 (3.46), and 296 nm (3.23); τ 6.80 (2H, m), 7.26 (2H, tt, $|J|$ 7 and 2 Hz) 7.78 (2H, t, $|J|$ 7 Hz), and 8.77 (6H, s) (Found: C, 65.7; H, 4.7%; M^+ , 256. $C_{14}H_{12}F_4$ requires C, 65.6; H, 4.7%; M , 256); and (ii) 4,5,6,7-tetrafluoro-2-isopropenylindene (19) (0.05 g, 13%), m.p. 76—78 °C (from methanol); τ 3.30 (1H, m), 4.74 (1H, m), 4.90 (1H, m), 6.36br (2H, s), and 7.95br (3H) (Found: M^+ , 228.0558. $C_{12}H_8F_4$ requires M , 228.0562).

Similarly compound (13) (1.5 g) gave an oil (0.9 g) which on chromatography gave two products: (i) 4,5,6,7-tetrachloro-1,2,3,8-tetrahydro-1,1-dimethylcyclopent[a]indene (17) (0.67 g, 45%), m.p. 153 °C (from ethanol); λ_{\max} (cyclohexane) 209 (log ϵ 4.22), 221 (4.28), 228 (4.33), 235 (4.35), 243 (4.28), 277 (4.22), and 287 nm (4.20); τ 6.85 (2H, m), 7.20 (2H, m), 7.82 (2H, m), and 8.78 (6H, s) (Found: C, 52.5; H, 3.8%; M^+ , 322. $C_{14}H_{12}Cl_4$ requires C, 52.5; H, 3.7%; M , 322); and (ii) 4,5,6,7-tetrachloro-2-isopropenylindene (20) (0.16 g, 11.5%), m.p. 145—146 °C (from ethanol); λ_{\max} (cyclohexane) 230 (log ϵ 4.19), 238 (4.21), 246 (4.25), 255 (4.13), 299 (4.34), 307 (4.37), and 319 nm (4.18); τ 3.29 (1H, m), 4.70 (1H, m), 4.90 (1H, m), 6.38br (2H), and 7.95br (3H) (Found: C, 48.6; H, 2.7%; M^+ , 294. $C_{12}H_8Cl_4$ requires C, 49.0; H, 2.7%; M , 294).

Compounds (1) and (9), treated under the foregoing conditions, were unchanged.

We thank the S.R.C. for a grant, and for 220 MHz n.m.r. spectra and accurate mass measurements through the P.C.M.U. We also thank the University and Hickson and Welch Ltd. (B. H.) and the Imperial Smelting Corporation (A. P. P.) for studentships.