

Aryne Chemistry. Part XXX.¹ Approaches to the Synthesis of 9-Alkyl- and 9,10-Dialkyl-1,2,3,4,5,6,7,8-octafluoro-9,10-dihydro-9,10-*o*-benzenoanthracenes (9-Alkyl- and 9,10-Dialkyl-1,2,3,4,5,6,7,8-octafluorotriptycenes)

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Two routes for the preparation of 2-methyl-5-*t*-butylfuran have been investigated; the reactions of tetrafluorobenzene with this furan and with 2-methyl- and 2,5-dimethyl-furan afforded the anticipated derivatives of 1,4-epoxy-5,6,7,8-tetrafluoro-1,4-dihydronaphthalene. The methyl-substituted adducts were elaborated, with butadiene, to give 9-methyl- and 9,10-dimethyl-1,2,3,4-tetrafluoro-5,6,7,8-tetrahydroanthracenes. Further reactions with tetrafluorobenzene, followed by dehydrogenation, afforded the title compounds.

PREVIOUS studies² have revealed examples of 'through-space' long-range ¹H-¹⁹F spin-spin coupling in the ¹H n.m.r. spectra in a number of different types of system. We have, in this connection, been particularly interested in the ¹H n.m.r. spectra of 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene (tetrafluorobenzo-barrelene) derivatives.³ We therefore investigated the synthesis of a number of 9-alkyl- and 9,10-dialkyl-1,2,3,4,5,6,7,8-octafluoro-9,10-dihydro-9,10-*o*-benzenoanthracenes (octafluorotriptycenes †).

Our proposed synthetic approach also involved the preparation of intermediates which would provide additional n.m.r. data. The reactions of tetrafluorobenzene with 2-alkyl- and 2,5-dialkyl-furans should afford 1,4-epoxy-1,4-dihydronaphthalene derivatives,⁴ which would be capable of being elaborated with buta-1,3-diene to tetrahydroanthracene derivatives.⁵ A number of potential routes would then be available to obtain the required *o*-benzenoanthracenes. The alkyl-

furans chosen as starting materials were 2-methylfuran, 2,5-dimethylfuran,⁶ and the previously unreported 2-methyl-5-*t*-butylfuran (1; R = H). Two routes to the last derivative were investigated.

The reaction of 1-bromo-3,3-dimethylbutanone with ethyl sodioacetoacetate (1.1 mol. equiv.) gave ethyl 2-acetyl-5,5-dimethyl-4-oxohexanoate (2; R = CO₂Et) in 80% yield, which, on hydrolysis with dilute aqueous sodium hydroxide, afforded 2,2-dimethylheptane-3,6-dione (2; R = H) in 66% yield. Dehydration of the diketone (2; R = H) with acetic anhydride gave the required furan (1; R = H) in 74% yield (overall yield from ethyl acetoacetate 39%). An attempted dehydration of the diketone (2; R = H) with zinc chloride in acetic anhydride, which is the method of choice for the preparation of 2,5-dimethylfuran,⁶ gave 3-acetyl-2-methyl-5-*t*-butylfuran (1; R = Ac) in 80% yield, presumably by Friedel-Crafts acetylation of the initially formed furan derivative (1; R = H). A comparison of the chemical shifts of the methyl resonances shown by the compound (1; R = Ac) with those for 3-acetyl-2,5-dimethylfuran and also those of the derived carbinol (1; R = CHMe-OH) and 1-(2,5-dimethyl-3-furyl)ethanol, both of which were obtained from the acetyl derivatives by reduction with sodium borohydride, established the

† Fully systematic names for triptycene derivatives are used in this paper.

¹ Part XXIX, H. Heaney, J. M. Jablonski, K. G. Mason, and J. M. Sketchley, *J. Chem. Soc. (C)*, 1971, 3129.

² D. R. Davis, R. P. Lutz, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1961, **83**, 246; M. Takahashi, D. R. Davis, and J. D. Roberts, *ibid.*, 1962, **84**, 2935; M. S. Newman, R. G. Mentzer, and G. Slomp, *ibid.*, 1963, **85**, 4018; A. H. Lewin, *ibid.*, 1964, **86**, 2303; A. D. Cross and P. W. Landis, *ibid.*, 1964, **86**, 4005, 4011; J. Burdon, *Tetrahedron*, 1965, **21**, 1101; P. C. Myhre, J. W. Edmonds, and J. D. Kruger, *J. Amer. Chem. Soc.*, 1966, **88**, 2459; R. J. Cushley, I. Wempen, and J. J. Fox, *ibid.*, 1968, **90**, 709; C. W. Jefford, D. T. Hill, L. Ghosez, S. Toppet, and K. C. Ramey, *ibid.*, 1969, **91**, 1532; R. Filler and E. W. Choe, *ibid.*, 1969, **91**, 1862; G. W. Gribble and J. R. Douglas, *ibid.*, 1970, **92**, 5764.

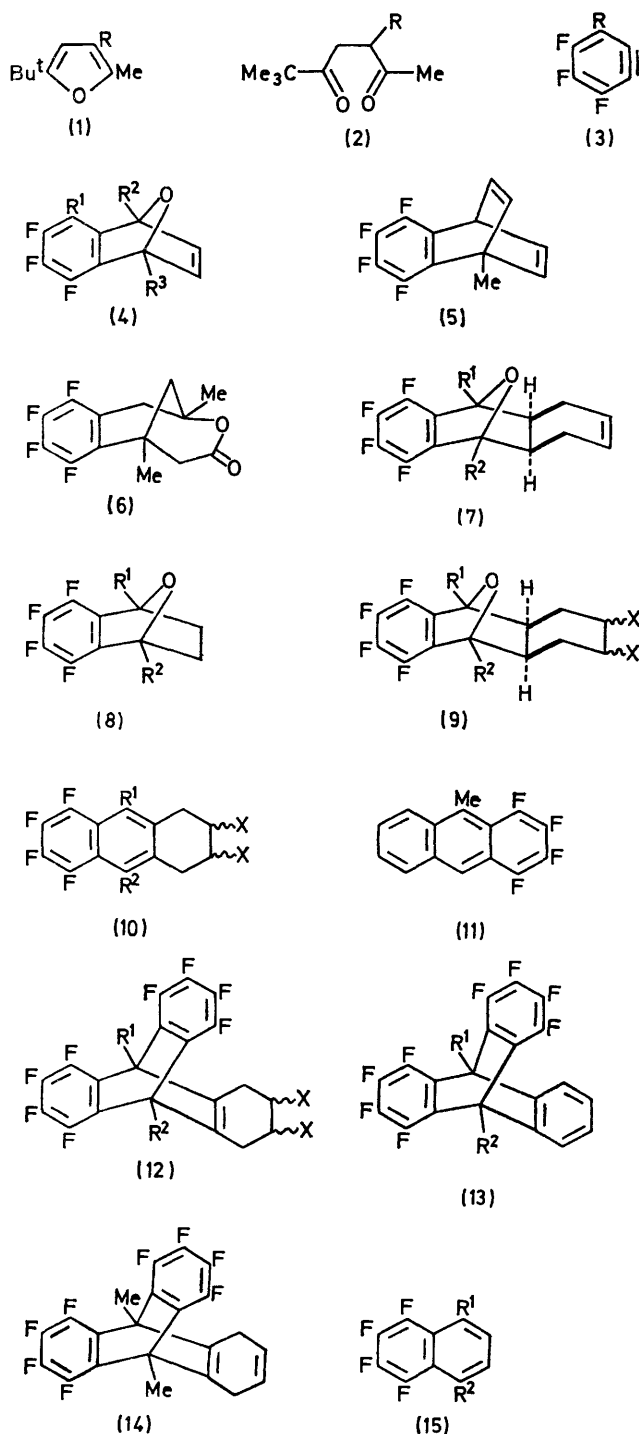
³ (a) J. P. N. Brewer, H. Heaney, and B. A. Marples, *Chem. Comm.*, 1967 27; (b) J. P. N. Brewer, I. F. Eckhard, H. Heaney, and B. A. Marples, *J. Chem. Soc. (C)*, 1968, 664.

⁴ R. W. Hoffmann, 'Dehydrobenzene and Cycloalkynes,' Academic Press New York 1967.

⁵ E. Wolthuis, *J. Org. Chem.*, 1961, **26**, 2215.

⁶ R. Gaertner and R. G. Tonkyn, *J. Amer. Chem. Soc.*, 1951, **73**, 5872.

structure of the acetylfuran. This result was further confirmed by use of the paramagnetic shift reagent



tris(dipivaloylmethanato)europium.⁷ The ΔE_u values^{7b} obtained were 1.95 for the 5-t-butyl resonance, 7.0 for

⁷ (a) C. C. Hinkley, *J. Amer. Chem. Soc.*, 1969, **91**, 5160; (b) P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *ibid.*, 1970, **92**, 5734; (c) J. M. K. Sanders and D. H. Williams, *ibid.*, 1971, **93**, 641; (d) H. Hart and G. M. Love, *Tetrahedron Letters*, 1971, 625; and references cited therein.

the 4-proton, 8.75 for the 2-methyl group, and 12.05 p.p.m. for the acetyl methyl group.

The ester (2; R = CO₂Et), when heated in ethanolic solution with a trace of hydrobromic acid, was converted rapidly into ethyl 2-methyl-5-t-butyl-3-furoate (1; R = CO₂Et) in high yield. In accord with this observation the reaction of ethyl sodioacetoacetate with 1-bromo-3,3-dimethylbutanone (1.05 mol. equiv.) gave the furan derivative (1; R = CO₂Et) directly in 76% yield. Hydrolysis of the ester (1; R = CO₂Et) and decarboxylation⁸ of the resulting acid (1; R = CO₂H) with copper(II) oxide in quinoline gave 2-methyl-5-t-butylfuran (1; R = H) in high yield (overall yield from ethyl acetoacetate, 58%).

Tetrafluorobenzene (3; R = F) is trapped efficiently by furan;⁹ 1,4-epoxy-5,6,7,8-tetrafluoro-1,4-dihydronaphthalene (4; R¹ = F, R² = R³ = H) was the only product detected when pentafluorophenyl-lithium was allowed to decompose in the presence of an approximately 30 molar excess of furan.¹⁰ We found that tetrafluorobenzene forms the expected adducts (4; R¹ = F, R² = Me, R³ = H, Me, or Bu^t) in high yield. However, since in our reactions we only used *ca.* 3 mol. equiv. of furan, some tetrafluorobenzene was trapped by its precursor, pentafluorophenyl-lithium. The resulting lithio-compound, 2-lithiononafluorobiphenyl, is itself an arylene precursor,¹¹ and can lose lithium fluoride to form 3-pentafluorophenyltrifluorobenzene (3; R = C₆F₅). Adducts derived from this arylene were isolated from the reaction mixtures by use of both 2-methyl- and 2,5-dimethyl-furan. In the latter case only one product derived from (3; R = C₆F₅) is possible and the structure of the product (4; R¹ = C₆F₅, R² = R³ = Me) was established from the elemental analysis and spectral data. In the reaction with 2-methylfuran two products derived from 3-pentafluorophenyltrifluorobenzene (4; R¹ = C₆F₅, R² = H, R³ = Me) and (4; R¹ = C₆F₅, R² = Me, R³ = H) were possible, and both were isolated. The structures of the isomers were evident from their ¹H n.m.r. data. In the case of the compound (4; R¹ = C₆F₅, R² = H, R³ = Me) the methyl resonance was observed as a singlet at τ 7.95, identical with the chemical shift of the methyl group in compound (4; R¹ = F, R² = Me, R³ = H). In the n.m.r. spectrum of the adduct (4; R¹ = C₆F₅, R² = Me, R³ = H) the methyl resonance was observed as a singlet at τ 8.52. Evidently the biphenyl system is twisted in this compound and the diamagnetic anisotropy of the C₆F₅ residue results in the methyl group experiencing an upfield shift of *ca.* 0.5 p.p.m. as compared with the

⁸ E. C. Wagner and J. K. Simons, *J. Chem. Educ.*, 1936 **13**, 265.

⁹ P. L. Coe, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 3227; G. A. Moser, F. E. Tibbitts, and M. D. Rausch, *Organometallic Chem. Synth.*, 1970, **1**, 99.

¹⁰ S. C. Cohen, M. L. N. Reddy, D. M. Roe, A. J. Tomlinson, and A. G. Massey, *J. Organometallic Chem.*, 1968, **14**, 241.

¹¹ D. E. Fenton and A. G. Massey, *Tetrahedron*, 1965, **21**, 3009; A. J. Tomlinson and A. G. Massey, *J. Organometallic Chem.*, 1967, **8**, 321; S. C. Cohen, A. J. Tomlinson, M. R. Wiles, and A. G. Massey, *ibid.*, 1968, **11**, 385.

isomeric compound. In agreement with this, the bridgehead protons in this pair of isomers resonate at positions which differ by *ca.* 0.6 p.p.m. The methyl resonances in the compound (4) in which a methyl group is in a *peri*-relationship to a fluorine atom are slightly broadened; they do not show the pronounced long-range ^{19}F - ^1H spin-spin coupling which is observed in the benzobarrelene derivatives. In the compound (5) $|^5J_{\text{HF}}|$ is 5.1 Hz.³ An analysis of the ^{19}F n.m.r. spectrum of compound (4; $\text{R}^1 = \text{Br}$, $\text{R}^2 = \text{R}^3 = \text{H}$) has been reported previously;¹² a coupling constant $|^4J_{\text{HF}}| = 2.5$ Hz was obtained. Long-range ^{19}F -H coupling is evidently not easily rationalised in these compounds. Molecular models indicate that, although the carbon-carbon bond from the bridgehead carbon atom to the methyl group in, for example, the adduct (4; $\text{R}^1 = \text{F}$, $\text{R}^2 = \text{Me}$, $\text{R}^3 = \text{H}$) is not co-planar with the *peri*-fluorine atom, the distance from a hydrogen atom to the *peri*-fluorine atom is not very much larger than the distance involved in compound (5). In addition we have observed long-range coupling between the *peri*-fluorine and bridgehead methyl groups in compounds such as (6).¹³ The absence of an appreciable ^{19}F - ^1H spin-spin coupling in the compounds (4) may be associated with the presence of the electronegative bridging group.

The compounds (4; $\text{R}^1 = \text{F}$, $\text{R}^2 = \text{Me}$, $\text{R}^3 = \text{H}$ or Me) gave quantitative yields of the Diels-Alder adducts (7; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$ or Me) when they were heated at 70 °C for 14 days in the presence of an excess of buta-1,3-diene. However, an analogous reaction with the compound (4; $\text{R}^1 = \text{F}$, $\text{R}^2 = \text{Me}$, $\text{R}^3 = \text{Bu}^t$) failed; starting material was recovered. The stereochemistry of compound (7; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$) can be assigned by a comparison of the n.m.r. behaviour of the bridgehead methine proton ($\text{R}^2 = \text{H}$) with that of the bridgehead methine proton in the compound (8; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$). In the former compound the bridgehead proton gave rise to a doublet, $|J_{\text{HH}(\text{endo})}|$ 1.7 Hz, while in the latter compound the bridgehead proton was observed as a doublet of doublets, $|J_{\text{HH}(\text{endo})}|$ 1.7, $|J_{\text{HH}(\text{exo})}|$ 6.2 Hz. In the compound under consideration the possibility that the coupling constant (1.7 Hz) is due to long-range coupling with fluorine can be ignored, since the expected magnitude of $|J_{\text{HH}(\text{endo})}|$ would be 0–2 Hz.¹⁴ The failure of the compound (4; $\text{R}^1 = \text{F}$, $\text{R}^2 = \text{Me}$, $\text{R}^3 = \text{Bu}^t$) to undergo a Diels-Alder reaction with buta-1,3-diene is therefore not completely unexpected since the transition state for the formation of such an adduct would involve the approach of the diene from the strongly hindered *exo*-face of the dienophile.

Attempts to convert the adducts (7) into anthracene derivatives directly, by use of chloranil, dichlorodicyanop-*p*-benzoquinone, or palladium-carbon, all failed. The compounds (7) were found, in common with the tetrahalogenobenzene-furan adducts,⁹ to be relatively re-

sistant to acid-catalysed ring opening and dehydration to 1,4-dihydroanthracene derivatives. When the compounds (7) were heated under reflux in acetic acid (or acetic anhydride) containing hydrobromic acid the expected dihydroanthracene derivatives were isolated. However, satisfactory analytical data could not be obtained owing to the presence of traces of bromine-containing impurities. The tetrahydroanthracene derivatives (10; $\text{R}^1 = \text{R}^2 = \text{Me}$, $\text{X} = \text{H}$ or Br, and $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$, $\text{X} = \text{H}$ or Br) were easily obtained from the compounds (9) but in the reaction of compound (9; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$, $\text{X} = \text{Br}$) we obtained, in addition to (10; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$, $\text{X} = \text{Br}$) (65%), the anthracene derivative (11) in 33% yield.

Each of the four tetrahydroanthracene derivatives (10) gave cycloadducts with tetrafluorobenzene. The aryne was generated from pentafluorophenylmagnesium chloride. In three of the four reactions we obtained the expected hexahydrobenzenoanthracene derivatives (12; $\text{R}^1 = \text{R}^2 = \text{Me}$, $\text{X} = \text{H}$ or Br and $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$, $\text{X} = \text{H}$), but in the reaction with the compound (10; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$, $\text{X} = \text{Br}$) we obtained the dihydrobenzenoanthracene (13; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$) directly. The compound (11) also gave (13; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$) in high yield. The compounds (12; $\text{R}^1 = \text{R}^2 = \text{Me}$, $\text{X} = \text{H}$ and $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{X} = \text{H}$) were dehydrogenated with palladium-carbon to the dihydrobenzenoanthracenes (13; $\text{R}^1 = \text{R}^2 = \text{Me}$ and $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$). A reaction of the hexahydro-derivative (12; $\text{R}^1 = \text{R}^2 = \text{Me}$, $\text{X} = \text{Br}$) with magnesium gave the expected tetrahydro-compound (14), and this was dehydrogenated to compound (13; $\text{R}^1 = \text{R}^2 = \text{Me}$).

The absence of pronounced long-range ^{19}F - ^1H spin-spin coupling which was noted in connection with the compounds (4) was also found in the majority of the other compounds which contain an oxygen bridge, *i.e.* compounds (7)–(9). The exceptions were compounds (4; $\text{R}^1 = \text{F}$, $\text{R}^2 = \text{Me}$, $\text{R}^3 = \text{Bu}^t$) and (8; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{Bu}^t$). In the remaining compounds, (10)–(15), pronounced long-range coupling was observed. In compounds (12)–(14) the methyl resonances were observed as the expected triplets ($|^5J_{\text{H-F}}|$ *ca.* 6 Hz). The naphthalene derivatives (15) also showed long-range ^{19}F - ^1H coupling and it is noteworthy that evidence for restricted rotation of the *t*-butyl group in (15; $\text{R}^1 = \text{Bu}^t$, $\text{R}^2 = \text{Me}$) was only observed in the n.m.r. spectrum at *ca.* –90 °C. This result will be reported in more detail later.

EXPERIMENTAL

The general methods used were reported in Part XXVIII,¹⁵ *Preparations of 2-Methyl-5-*t*-butylfuran.*—Ethyl acetate (38.8 g) was added to a solution of sodium ethoxide [from ethanol (150 ml) and sodium (6.8 g)], and 1-bromo-

¹² C. Tamborski and E. J. Soloski, *J. Organometallic Chem.*, 1967, **10**, 385.

¹³ H. Heaney and S. V. Ley, *Chem. Comm.*, 1971, 1342; and unpublished observations.

¹⁴ L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd., edn., Pergamon, Oxford, 1969, p. 283.

¹⁵ H. Heaney, K. G. Mason, and J. M. Sketchley, *J. Chem. Soc. (C)*, 1971, 567.

3,3-dimethylbutan-2-one¹⁶ (53 g) was added slowly. The mixture was heated under reflux for 64 h and the solvent was removed. The residue was washed with water and dried and gave *ethyl 2-acetyl-5,5-dimethyl-4-oxohexanoate* (2; R = CO₂Et), b.p. 98–100° at 0.8 mmHg (54.15 g, 80.5%); ν_{\max} , 1752, 1728, and 1718 cm⁻¹; τ 5.86 (q, |J| 6 Hz, O·CH₂·CH₃), 6.07 (m, CH·CH₂, X of ABX), 7.00 (O·CH₂·CH₂, AB of ABX), 7.70 (s, Ac), 8.74 (t, |J| 6 Hz, CH₂·CH₃), and 8.86 (s, Bu^t) (Found: C, 62.95; H, 8.75. C₁₂H₂₀O₄ requires C, 63.15; H, 8.85%).

The reaction was repeated with identical quantities except for sodium (6.5 g) and gave *ethyl 2-methyl-5-t-butyl-3-furoate* (1; R = CO₂Et), b.p. 80° at 0.9 mmHg (75.8%); ν_{\max} , 1725 cm⁻¹; λ_{\max} (EtOH) 254 nm (log ϵ 3.60); τ 3.80 (s, CH), 5.74 (q, |J| 7 Hz, O·CH₂·CH₃), 7.43 (s, CH₃), 8.67 (t, |J| 7 Hz, CH₂·CH₃), and 8.73 (s, Bu^t) (Found: C, 68.65; H, 8.65. C₁₂H₁₈O₃ requires C, 68.55; H, 8.65%).

The ester (2; R = CO₂Et) (50 g) was stirred for 4 h at room temperature with an excess of aqueous 5% sodium hydroxide (10.9 g sodium hydroxide). The aqueous layer was carefully acidified with sulphuric acid and then distilled until the volume had been reduced by one half. The distillate was extracted with ether, dried, and gave on distillation *2,2-dimethylheptane-3,6-dione* (2; R = H), b.p. 80–82° at 8 mmHg (22.7 g, 66.5%); ν_{\max} , 1728 and 1715 cm⁻¹; τ 7.32 (s, CH₂ × 2), 7.92 (s, CH₃), and 8.87 (s, Bu^t) (Found: C, 69.1; H, 10.6. C₉H₁₆O₂ requires C, 69.2; H, 10.3%).

Acetic anhydride (40 ml) containing anhydrous zinc chloride (1.5 g) was added slowly to the diketone (2; R = H) (20 g). An exothermic reaction ensued and the mixture was finally heated under reflux for 3 h. The cold mixture was added to water, made alkaline with sodium hydroxide, and distilled in steam to give *3-acetyl-2-methyl-5-t-butylfuran* (1; R = Ac), b.p. 106–108° at 15 mmHg, m.p. 39–40° (79.5%); ν_{\max} , 1688 cm⁻¹; λ_{\max} (EtOH) 276 nm (log ϵ 3.72); τ 3.85 (s, CH), 7.49 (s, CH₃), 7.73 (s, Ac), and 8.73 (s, Bu^t) (Found: C, 73.05; H, 9.05. C₁₁H₁₆O₂ requires C, 73.3; H, 8.95%).

The ketone (1; R = Ac) (1.8 g) in methanol (20 ml) was stirred for 3 h at room temperature with sodium borohydride (0.42 g) and gave *1-(2-methyl-5-t-butyl-3-furyl)ethanol* (1; R = MeCH₂OH), m.p. 57.5–59° (from hexane) (98%); ν_{\max} , 3300 cm⁻¹; τ 3.99 (s, CH), 5.16 [q, |J| 6.8 Hz, CH(OH)·CH₂], 7.76 (s, CH₃), 8.06br (OH, exchangeable), 8.60 [d, |J| 6.8 Hz, CH(OH)·CH₂], and 8.77 (s, Bu^t) (Found: C, 72.25; H, 9.9. C₁₁H₁₈O₂ requires C, 72.5; H, 9.95%).

*3-Acetyl-2,5-dimethylfuran*¹⁷ [τ 3.79 (s, CH), 7.51 (s, CH₃), 7.73 (s, Ac), and 7.75 (s, Me) was similarly reduced with sodium borohydride and gave *1-(2,5-dimethyl-3-furyl)ethanol*, b.p. 80–82° at 2 mmHg (90%); ν_{\max} , 3400 cm⁻¹; τ 4.21 (s, CH), 5.45 [q, CH(OH)·CH₂, |J| 6.6 Hz], 6.05br (OH, exchangeable), 7.87 (s, 2 × CH₃), and 8.75 [d, CH(OH)·CH₂, |J| 6.6 Hz]; λ_{\max} (EtOH) 221 nm (log ϵ 3.77); m/e 140.0839 (*M*⁺) (C₉H₁₂O₂ requires *M*, 140.0837).

The diketone (2; R = H) (12 g) was heated under reflux in acetic anhydride (30 ml) for 5 h. Addition to aqueous sodium hydroxide and distillation in steam gave, after extraction and distillation, *2-methyl-5-t-butylfuran* (1; R = H), b.p. 140° (73.5%); λ_{\max} (EtOH) 272 nm (log ϵ 2.75); τ 4.29 (s, 2 × CH), 7.82 (s, CH₃), and 8.78 (s, Bu^t) (Found: C, 78.25; H, 10.4. C₉H₁₄O requires C, 78.2; H, 10.2%).

The ester (1; R = CO₂Et) (50 g) was heated under reflux

in aqueous ethanolic (2 : 1; 600 ml) 20% sodium hydroxide for 20 h and gave, after acidification, *2-methyl-5-t-butyl-3-furoic acid* (1; R = CO₂H), m.p. 88–92° (94.8%); ν_{\max} , 1700 cm⁻¹; λ_{\max} (EtOH) 253 nm (log ϵ 3.68); τ 2.87 (s, CO₂H, exchangeable), 3.80 (s, CH), 7.45 (s, CH₃), and 8.76 (s, Bu^t) (Found: C, 65.8; H, 7.95. C₁₀H₁₄O₃ requires C, 65.9; H, 7.75%).

Copper(II) oxide (3 g) was added to a solution of the acid (1; R = CO₂H) (45 g) in quinoline (160 ml) and the mixture was heated to 200 °C. Fractionation through a Vigreux column gave *2-methyl-5-t-butylfuran* (1; R = H), b.p. 140° (80.5%), identical with previously isolated material.

Reactions of Arynes with Alkylfurans.—2-Methylfuran. Butyl-lithium (25 ml, 0.06 mol) was added to a solution of bromopentafluorobenzene (12.4 g, 0.05 mol) in ether (100 ml) at –70°. After 0.5 h *2-methylfuran* (12.3 g, 0.15 mol) in ether (30 ml) was added. The mixture was allowed to warm to room temperature and after 12 h was washed with dilute hydrochloric acid and water, dried, and evaporated. The residue gave, on distillation, *1,4-epoxy-5,6,7,8-tetrafluoro-1,4-dihydro-1-methylnaphthalene* (4; R¹ = F, R² = Me, R³ = H), b.p. 50–52° at 0.3 mmHg, m.p. 26–28° (8.1 g, 70%); τ 2.8–3.15 (m, CH:CH), 4.1 (t, CH), and 7.95 (s, CH₃) (Found: C, 57.55; H, 2.85. C₁₁H₆F₄O requires C, 57.4; H, 2.65%).

Preparative layer chromatography of the distillation residue gave *1,4-epoxy-6,7,8-trifluoro-1,4-dihydro-1-methyl-5-pentafluorophenylnaphthalene* (4; R¹ = C₆F₅, R² = H, R³ = Me) (1 g, 5%), m.p. 130° (from light petroleum); τ 2.8–3.15 (m, CH:CH), 4.65 (m, CH), and 7.95 (s, CH₃); m/e 378, 362, 352, and 335 (Found: C, 53.95; H, 2.0%; *M*⁺, 378. C₁₇H₆F₈O requires C, 53.9; H, 1.6%; *M*, 378); and *1,4-epoxy-5,6,7-trifluoro-1,4-dihydro-1-methyl-8-pentafluorophenylnaphthalene* (4; R¹ = C₆F₅, R² = Me, R³ = H) (0.5 g, 2.5%), m.p. 148–150° (from hexane); τ 2.7–3.2 (m, CH:CH), 4.05 (m, CH), and 8.52 (s, CH₃); m/e 378, 362, 352, and 335 (Found: C, 54.1; H, 1.65%; *M*⁺, 378).

2,5-Dimethylfuran. Similarly we obtained *1,4-epoxy-5,6,7,8-tetrafluoro-1,4-dihydro-1,4-dimethylnaphthalene* (4; R¹ = F, R² = R³ = Me), b.p. 56–58° at 0.3 mmHg, m.p. 52–54° (67.5%); τ 3.1 (m, CH:CH) and 8.0 (s, CH₂ × 2); m/e 244, 229, 218, and 203 (Found: C, 58.85; H, 3.45%; *M*⁺, 244. C₁₂H₆F₄O requires C, 59.0; H, 3.3%; *M*, 244); and *1,4-epoxy-5,6,7-trifluoro-1,4-dihydro-1,4-dimethyl-8-pentafluorophenylnaphthalene* (4; R¹ = C₆F₅, R² = R³ = Me) (1.8 g, 10%), m.p. 140–141° (from light petroleum); τ 3.1 (s, CH:CH), 7.95 (s, CH₃), and 8.55 (s, CH₃); m/e 392, 376, 366, 349, 329, 310, 279, and 273 (Found: C, 55.0; H, 2.1%; *M*⁺, 392. C₁₈H₈F₈O requires C, 55.1; H, 2.05%; *M*, 392).

2-Methyl-5-t-butylfuran. This gave *1,4-epoxy-5,6,7,8-tetrafluoro-1,4-dihydro-1-methyl-4-t-butyl-naphthalene* (4; R¹ = F, R² = Bu^t, R³ = Me) (58%), b.p. 140° at 2 mmHg; τ 3.15 (m, CH:CH), 8.03 (d, CH₃, |J|_{HF} 1.1 Hz), and 8.78 (d, Bu^t, |J|_{HF} 0.7 Hz) (Found: C, 62.8; H, 4.7. C₁₅H₁₄F₄O requires C, 62.95; H, 4.95%).

*Conversions into 5,6,7,8-Tetrafluoronaphthalene Derivatives.—(a) Hydrogenation of compound (4; R¹ = F, R² = Me, R³ = H) in ethanol at atmospheric pressure over palladium-carbon gave *1,4-epoxy-5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-1-methylnaphthalene* (8; R¹ = Me, R² = H) (100%), m.p. 36.5–37°; τ 4.45 (dd, CH), 8.07–8.75 (m, CH₂·CH₂), and 8.12 (s, CH₃) (Found: C, 56.85; H, 3.45.*

¹⁶ J. H. Boyer and D. Straw, *J. Amer. Chem. Soc.*, 1952, **74**, 4506.

¹⁷ H. Gilman and R. R. Burtner, *J. Amer. Chem. Soc.*, 1935, **57**, 909.

$C_{11}H_5F_4O$ requires C, 56.9; H, 3.45%). The compound (8; $R^1 = Me$, $R^2 = H$) was heated under reflux in acetic anhydride containing hydrobromic acid (10% v/v) for 12 h and gave 1,2,3,4-tetrafluoro-5-methylnaphthalene (95%), m.p. and mixed m.p. 95–97° (lit.,^{3b} 95–97°), i.r. spectra identical.

(b) The compound (4; $R^1 = F$, $R^2 = R^3 = Me$) gave 1,4-epoxy-5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-1,4-dimethylnaphthalene (8; $R^1 = R^2 = Me$) (100%), m.p. 80–81° (Found: C, 58.45; H, 3.95. $C_{12}H_{10}F_4O$ requires C, 58.55; H, 4.1%); τ 7.94–8.60 (m, $CH_2 \cdot CH_2$) and 8.17 (s, $CH_3 \times 2$); and hence 1,2,3,4-tetrafluoro-5,8-dimethylnaphthalene (15; $R^1 = R^2 = Me$) (48%), m.p. 124–127° (Found: C, 63.25; H, 3.5. $C_{12}H_8F_4$ requires C, 63.15; H, 3.55%); τ 2.99 (s, CH) and 7.3–7.45 (m, CH_3 , $|J|_{HF}$ ca. 9 Hz); λ_{max} 286 (log ϵ 3.86), 311 (3.39), 321 (3.27), and 325 (3.40) nm.

(c) The compound (4; $R^1 = F$, $R^2 = Me$, $R^3 = Bu^t$) gave 1,4-epoxy-5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-1-methyl-4-*t*-butylnaphthalene (8; $R^1 = Me$, $R^2 = Bu^t$) (100%), b.p. 140° at 2 mmHg (Found: C, 62.7; H, 5.55. $C_{15}H_{16}F_4O$ requires C, 62.5; H, 5.6%); τ 7.80–8.94 (m, $CH_2 \cdot CH_2$), 8.13 (d, CH_3 , $|J|_{HF}$ 1.4 Hz), and 8.85 (d, Bu^t , $|J|_{HF}$ 0.6 Hz) and hence 1,2,3,4-tetrafluoro-5-methyl-8-*t*-butylnaphthalene (15; $R^1 = Bu^t$, $R^2 = Me$), m.p. 99.5–100° (Found: C, 66.95; H, 5.35. $C_{15}H_{14}F_4$ requires C, 66.65; H, 5.2%); λ_{max} 287 (log ϵ 3.82), 295 (3.74), 310 (3.29), 320 (3.11), and 325 (3.20) nm; τ 2.64 (dd, $|J|$ 8.0 Hz), 7.24 (d, $|J|_{HF}$ 10.0 Hz), and 8.50 (d, $|J|_{HF}$ 4.0 Hz).

Reactions with Buta-1,3-diene.—(a) A mixture of compound (4; $R^1 = F$, $R^2 = Me$, $R^3 = H$) (2 g), hydroquinone (10 mg), and buta-1,3-diene (2 g) was heated in a sealed tube for 14 days at 70° and gave 9,10-epoxy-5,6,7,8-tetrafluoro-1,4,4a,9,9a,10-hexahydro-9-methylanthracene (7; $R^1 = Me$, $R^2 = H$) (98%), m.p. 62–63° (from methanol) (Found: C, 63.1; H, 4.3. $C_{15}H_{12}F_4O$ requires C, 63.4; H, 4.25%); τ 4.01–4.13 (m, $CH \cdot CH$), 4.94 (d, CH bridgehead, $|J|$ 1.7 Hz), 7.37–8.20 (m, CH_2 and CH), and 8.22 (s, CH_3); and hence 9,10-epoxy-5,6,7,8-tetrafluoro-1,2,3,4,4a,9,9a,10-octahydro-9-methylanthracene (9; $R^1 = Me$, $R^2 = H$, X = H) (100%), m.p. 74.5–75° (Found: C, 63.0; H, 4.95. $C_{15}H_{14}F_4O$ requires C, 62.95; H, 4.95%); τ 4.95 (d, $|J|$ 1.7 Hz, CH), 8.25 (s, CH_3), and 8.4 (complex m, CH_2 and CH). Compound (7; $R^1 = Me$, $R^2 = H$) (5.0 g) in carbon tetrachloride was treated with a solution of bromine (3 g) in carbon tetrachloride. Work-up after 4 h gave a mixture of isomeric dibromides (9; $R^1 = Me$, $R^2 = H$, X = Br) (7.7 g, 97%), m.p. 116–121° (from benzene), *m/e* 446, 444, and 442; τ 4.82 (m, CH), 5.17 (m, CH), 5.65 (m, CH), 7.85 (m, 6H), and 8.18 (s, CH_3).

(b) Compound (4; $R^1 = F$, $R^2 = R^3 = Me$) gave, with butadiene, 9,10-epoxy-5,6,7,8-tetrafluoro-1,4,4a,9,9a,10-hexahydro-9,10-dimethylanthracene (7; $R^1 = R^2 = Me$) (100%), m.p. 92–93° (from methanol) (Found: C, 64.65; H, 4.75%; M^+ , 298. $C_{16}H_{14}F_4O$ requires C, 64.45; H, 4.75%; M , 298); τ 3.97–4.1 (m, $CH \cdot CH$), 7.55–8.20 (m, CH_2 and CH), and 8.25 (s, CH_3); and hence 9,10-epoxy-5,6,7,8-tetrafluoro-1,2,3,4,4a,9,9a,10-octahydro-9,10-dimethylanthracene (9; $R^1 = R^2 = Me$, X = H) (100%), m.p. 130–131° (from hexane) (Found: C, 64.2; H, 5.3. $C_{16}H_{16}F_4O$ requires C, 64.0; H, 5.35%); τ 8.28 (s, CH_3) and 8.4 (m, CH_2 and CH). Compound (7; $R^1 = R^2 = Me$) gave the dibromides (9; $R^1 = R^2 = Me$, X = Br) (99.5%), m.p. 120–122° (from benzene); *m/e* 460, 458, and 456; τ 5.2 (m, CH), 5.75 (m, CH), 7.8–8.1 (m, 6H), and 8.2 (s, CH_3).

Conversion of the Octahydroanthracenes into Tetrahydro-

anthracenes.—Compound (9; $R^1 = Me$, $R^2 = H$, X = H) (100 mg) was heated under reflux for 4 h in acetic anhydride (25 ml) containing hydrobromic acid (5 ml) and gave, on dilution with water, 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-methylanthracene (10; $R^1 = Me$, $R^2 = H$, X = H), m.p. 119–120° (95%) (Found: C, 67.3; H, 4.4. $C_{15}H_{12}F_4$ requires C, 67.15; H, 4.5%); λ_{max} (EtOH) 271 (log ϵ 3.56), 281 (3.68), 290 (3.71), 299 (3.58), and 325 (2.73) nm; τ 2.46 (m, 1H), 7.41 (d, CH_3 , $|J|_{HF}$ 6.0 Hz), 7.02–7.25 (m, $CH_2 \times 2$), and 8.10–8.35 (m, $CH_2 \cdot CH_2$).

Compound (9; $R^1 = Me$, $R^2 = H$, X = Br) (5.2 g) in acetic acid (70 ml) and hydrobromic acid (11 ml) was heated under reflux for 12 h and gave a mixture which was separated by chromatography on silica to afford (a) 1,2,3,4-tetrafluoro-9-methylanthracene (11), m.p. 239° (from light petroleum) (1.0 g, 33%); λ_{max} (cyclohexane) 347 (log ϵ 3.93), 366 (4.10), and 386 (4.01) nm; τ 1.6–3.5 (m, 5H) and 7.35 (d, CH_3 , $|J|_{HF}$ 6.0 Hz); *m/e* 264; and (b) the tetrahydroanthracene (10; $R^1 = Me$, $R^2 = H$, X = Br), m.p. 150–151° (from benzene) (3.2 g, 65%); λ_{max} (cyclohexane) 281 (log ϵ 3.75), 291 (3.77), and 302 (3.64) nm; τ 2.28br (s, 1H), 5.12 (m, $CHBr \times 2$), 5.5–6.8 (m, $CH_2 \times 2$), and 7.28 (d, CH_3 , $|J|_{HF}$ 5.1 Hz); *m/e* 428, 426, and 424.

Compound (9; $R^1 = R^2 = Me$, X = H) gave 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9,10-dimethylanthracene (10; $R^1 = R^2 = Me$, X = H), m.p. 196–198° (92%) (Found: C, 68.2; H, 5.1. $C_{16}H_{14}F_4$ requires C, 68.1; H, 5.0%); λ_{max} (EtOH) 287 (log ϵ 3.72), 296 (3.74), and 331 (3.11) nm; τ 7.05–7.25 (m, $CH_2 \times 2$), 7.32–7.45 (m, $CH_3 \times 2$), and 8.06–8.30 (m, $CH_2 \cdot CH_2$).

Compound (9; $R^1 = R^2 = Me$, X = Br) gave the tetrahydroanthracene (10; $R^1 = R^2 = Me$, X = Br), m.p. 226–227° (1.6 g, 84%); λ_{max} (cyclohexane) 286 (log ϵ 3.72) and 297 (3.75) nm; *m/e* 442, 440, and 438.

Preparation of Octafluorodihydrobenzenoanthracene Derivatives.—(a) From 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-methylanthracene. The compound (10; $R^1 = Me$, $R^2 = X = H$) (0.4 g, 1.5 mmol) in cyclohexane (30 ml) was added to a solution of pentafluorophenylmagnesium chloride [from chloropentafluorobenzene (0.5 g, 2.5 mmol)] in ether and the ether was replaced with cyclohexane by distillation until the temperature of the distillate reached 80 °C. The mixture was then heated under reflux for 5 h. After a further 12 h the mixture was acidified with hydrochloric acid (4N) and the aqueous layer was extracted with ether. The combined organic layers were dried and concentrated and the residue was placed on a column of silica. Elution with light petroleum gave 1,2,3,4,5,6,7,8-octafluoro-9,10,13,14,15,16-hexahydro-9-methyl-9,10-o-benzenoanthracene (12; $R^1 = Me$, $R^2 = X = H$), m.p. 238–240° (from light petroleum) (0.3 g, 50%) (Found: C, 60.3; H, 2.95%; M^+ , 416. $C_{21}H_{12}F_8$ requires C, 60.6; H, 2.9%; M , 416); λ_{max} (EtOH) 258 nm (log ϵ 3.09); τ 4.57 (t, C-H, $|J|_{HF}$ 1.6 Hz), 7.62 (t, CH_3 , $|J|_{HF}$ 6.0 Hz), 7.75 (m, $CH_2 \times 2$), and 8.5 (m, $CH_2 \cdot CH_2$). Compound (12; $R^1 = Me$, $R^2 = X = H$) (88 mg) was heated with palladium (10% on carbon; 60 mg) at 250 °C under nitrogen for ca. 4 h. The cold residue was extracted with ether and gave 1,2,3,4,5,6,7,8-octafluoro-9,10-dihydro-9-methyl-9,10-o-benzenoanthracene (13; $R^1 = Me$, $R^2 = H$), m.p. 204–205° (from light petroleum) (48 mg, 56%) (Found: C, 61.25; H, 2.0%; M^+ , 412. $C_{21}H_8F_8$ requires C, 61.15; H, 1.95%; M , 412); τ 2.3–2.9 (m, 4H), 3.8 (t, CH, $|J|_{HF}$ 1.6 Hz), and 7.25 (t, CH_3 , $|J|_{HF}$ 5.95 Hz).

(b) From 2,3-dibromo-5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-methylanthracene. Compound (10; $R^1 = Me$, $R^2 = H$,

X = Br) (1.9 mmol) and chloropentafluorobenzene (10.0 mmol) gave 1,2,3,4,5,6,7,8-octafluoro-9,10-dihydro-9-methyl-9,10-*o*-benzenoanthracene (13; R¹ = Me, R² = H) (55%), m.p. and mixed m.p. 204—205°; i.r. spectra identical.

(c) From 1,2,3,4-tetrafluoro-9-methylanthracene. Compound (11) (3 mmol) and chloropentafluorobenzene (10 mmol) gave 1,2,3,4,5,6,7,8-octafluoro-9,10-dihydro-9-methyl-9,10-*o*-benzenoanthracene (13; R¹ = Me, R² = H) (60%), m.p. and mixed m.p. 204—205°; i.r. spectra identical.

(d) From 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9,10-dimethylanthracene. Compound (10; R¹ = R² = Me, X = H) (20 mmol) and chloropentafluorobenzene (40 mmol) gave 1,2,3,4,5,6,7,8-octafluoro-9,10,13,14,15,16-hexahydro-9,10-dimethyl-9,10-*o*-benzenoanthracene (12; R¹ = R² = Me, X = H), m.p. 262—265° (sublimes) (from hexane) (58%) (Found: C, 61.3; H, 3.4%; M⁺, 430. C₂₂H₁₄F₈ requires C, 61.4; H, 3.3%; M, 430); τ 7.55—7.90 (m, 2 × CH₃ and 2 × CH₂) and 8.40—8.60 (m, CH₂·CH₂).

Compound (12; R¹ = R² = Me, X = H) was dehydrogenated with palladium-carbon and gave 1,2,3,4,5,6,7,8-octafluoro-9,10-dihydro-9,10-dimethyl-9,10-*o*-benzenoanthracene (13; R¹ = R² = Me), m.p. 225—227° (from light petroleum) (72%) (Found: C, 62.1; H, 2.45%; M⁺, 426.

C₂₂H₁₀F₈ requires C, 61.95; H, 2.35%; M, 426); τ 2.38—2.95 (m, 4H) and 7.30 (m, 2 × CH₃, |J_{HF}| 6 Hz).

(e) From 2,3-dibromo-5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9,10-dimethylanthracene. Compound (10; R¹ = R² = Me, X = Br) (2.0 mmol) and chloropentafluorobenzene (5.0 mmol) gave, after chromatography on silica, 14,15-dibromo-1,2,3,4,5,6,7,8-octafluoro-9,10-dihydro-9,10-dimethyl-9,10-*o*-benzenoanthracene (12; R¹ = R² = Me, X = Br), m.p. 201—204° (from light petroleum) (60%); τ 5.5br (s, 2 × CH), 6.45—7.35 (m, 2 × CH₂), and 7.65 (t, 2 × CH₃, |J_{HF}| 6.35 Hz); m/e 590, 588, and 586. Compound (12; R¹ = R² = Me, X = Br) (0.2 mmol) reacted with magnesium in ether and cyclohexane to give (after work-up) compound (14), m.p. 240—243° (from light petroleum) (85%); τ 4.32 (s, CH:CH), 7.05 (s, 2 × CH₂), and 7.62 (t, 2 × CH₃, |J_{HF}| 6 Hz); m/e 428. Compound (14) was dehydrogenated to the benzenoanthracene (13; R¹ = R² = Me) with palladium (66%); m.p. and mixed m.p. 225—228°; i.r. spectra identical.

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