

product was particularly difficult to characterise, owing to its instability. For example a sample was *ca.* 90% polymerised after 24 h under nitrogen at -25° . No stable examples of 4a,8b-dihydrobiphenylenes appear to be known;⁷ usually such compounds undergo valence-bond isomerisation to the thermally more stable benzocyclo-octenes.⁸ However, the product (c) was eventually shown to be the benzocyclo-octene (5) and its tetrahydro-derivative the compound (6). It is significant that we were unable to form Diels–Alder adducts with compound (5), nor were we able to prepare an *N*-oxide or a quaternary salt. Neither compound (5) nor its tetrahydro-derivative (6) was affected by being heated for a brief period in the presence of mineral acid. Similarly compound (6) was not reduced by sodium borohydride in methanolic solution. These results initially suggested that compounds (5) and (6) were not enamines. The u.v. spectrum of compound (5) showed λ_{max} 263 nm (ϵ 7000), the ^1H n.m.r. spectrum had resonances at τ 3.38–4.5 (4H), 5.15 (1H), and 7.42 (6H), and the mass spectrum showed significant peaks at *m/e* 269, 254, 240, 225, and 224. The u.v. spectrum could be due to a benzocyclo-octene chromophore.^{8a} Both compounds (5) and (6) showed strong peaks in their i.r. spectra at *ca.* 1650 cm^{-1} which are characteristic of enamines.⁹

In the ^1H n.m.r. spectrum of compound (5) a quartet (1H) centred at τ 3.53 ($|J|$ 12 and 1.5 Hz) is analogous to the doublet associated with the protons adjacent to the benzo-ring in benzocyclo-octene (τ 3.49; $|J|$ 12 Hz).¹⁰ The additional coupling (1.5 Hz) is presumably due to long-range ^{19}F ,H interaction, since in the tetrachloro-analogue (7) we only observed a doublet at τ 3.49 ($|J|$ 12 Hz). Compound (5) and its tetrachloro-analogue (7) also showed broadened doublets in the ^1H n.m.r. spectra at τ *ca.* 5.21 ($|J|$ 3 Hz), in good accord with reported chemical shifts for enamine vinylic protons.⁹ *NN*-Dimethylcyclo-octatetraenylamine, reported recently,^{9b} shows resonances at τ 4.2 (6H, d), 5.6 (1H, d), and 7.4 (6H, s). It is described as a yellow oil, like many derivatives of this ring system, and satisfactory elemental analyses were not obtained.

An alternative synthesis of the benzocyclo-octene (5) was attempted *via* the unsensitised photoisomerisation of the benzobarrelele (1), although this was expected¹¹ to give a mixture of products. Photoisomerisation of compound (1) with a Hanovia medium-pressure source (450 W) in light petroleum gave, after an incomplete reaction, much polymeric material together with unchanged starting material (30%), compound (5) (6%),

and a product tentatively identified as the benzosemi-bullvalene (9) (2%).

Our difficulty in fully characterising the products formed by 1,2-cycloaddition of tetrahalogenobenzynes with *NN*-dimethylaniline was due to their great propensity towards polymerisation. We therefore concentrated on the more stable tetrahydro-derivatives. For comparison with compound (6), the dimethylamino-benzocyclobutene (10) was prepared by the reaction of tetrafluorobenzynes with *NN*-dimethylcyclohex-1-enylamine. The comparison showed that the compounds were not identical, and further that they could not be epimers. We originally reported² that the tetrahydro-derivative (6) was recovered after being heated with mineral acid for a brief period. However, when we heated this substance for 6 h in aqueous ethanol containing a trace of hydrochloric acid we obtained a quantitative yield of a ketone, λ_{max} 264 nm (ϵ 660), ν_{max} 1710 cm^{-1} (C=O). Although this i.r. frequency is high for a normal aryl ketone¹² it is not unusual in polyfluoroaryl carbonyl compounds.¹³ ^1H N.m.r. spectroscopy showed the presence of methylene groups adjacent to aryl and carbonyl residues [τ 7.1–7.5 (4H)] and other methylene resonances at τ 8.0–8.5 (6H). The noise-decoupled ^{13}C n.m.r. spectrum showed resonances (downfield from Me_4Si) at 193.5, 46.9, 27.5, 26.6, 24.2, and 23.1 p.p.m. The resonance at 46.9 p.p.m. was confirmed as due to a benzylic carbon atom by its observation as a triplet ($|J|$ 135 Hz) in the undecoupled spectrum. The absence of resonances due to the aromatic carbon atoms was presumably due to the presence of ^{13}C , ^{19}F coupling and to long relaxation times. These data are in accord with published values¹⁴ and allow us to assign structure (11) to the ketone. This structure was confirmed by base-catalysed hydrogen exchange in dioxan containing deuterium oxide,¹⁵ which led to the incorporation of two deuterium atoms.

The stability of the enamine (6) towards hydrolysis and towards reduction by sodium borohydride in methanol must be due to the electron-withdrawing effect of the tetrafluorobenzo-residue. This makes C-protonation more difficult than with normal enamines. In accord with this, treatment of the enamine (6) with sodium borohydride in tetrahydrofuran to which we added an excess of glacial acetic acid gave a good yield of the amine (12).

Analogous benzocyclo-octene derivatives were

⁷ M. P. Cava and M. J. Mitchell, 'Cyclobutadiene and Related Compounds,' Academic Press, New York, 1967; J. W. Barton, in 'Nonbenzenoid Aromatics, I,' ed. J. P. Snyder, Academic Press, New York, 1969.

⁸ (a) J. W. Barton and K. E. Whitaker, *J. Chem. Soc. (C)*, 1968, 1663; (b) A. J. Boulton and J. F. W. McOmie, *J. Chem. Soc.*, 1965, 2549.

⁹ (a) A. G. Cook, 'Enamines: Synthesis, Structure, and Reactions,' Dekker, New York, 1969; (b) C. A. Harmon and A. Streitwieser, *J. Org. Chem.*, 1973, **38**, 549.

¹⁰ J. A. Elix and M. V. Sargent, *J. Amer. Chem. Soc.*, 1969, **91**, 4734.

¹¹ J. P. N. Brewer and H. Heaney, *Chem. Comm.*, 1967, 811; 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; H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Amer. Chem. Soc.*, 1968, **90**, 6096.

¹² L. J. Bellamy, 'The Infra-red Spectra of Complex Molecules,' Methuen, London, 1958, p. 132.

¹³ S. S. Dua, A. E. Jukes, and H. Gilman, *Organometallics in Chem. Synth.*, 1970, **1**, 87; J. K. Brown and K. J. Morgan in 'Advances in Fluorine Chemistry,' eds. M. Stacy, J. C. Tatlow, and A. G. Sharpe, Butterworths, London, 1965.

¹⁴ J. B. Stothers, 'Carbon-13 N.M.R. Spectroscopy,' Academic Press, New York, 1972; G. C. Levy and G. L. Nelson, 'Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley-Interscience, New York, 1972.

¹⁵ J. Sato, K. Murata, and A. Nichimura, *Tetrahedron*, 1967, **23**, 1791.

stabilised by solvation, whereas in ether it can be more easily solvated and hence can form the ylide (17). However, it is noteworthy that *N*-methyl-*N*-*p*-tolyltetrafluoro-*o*-toluidine was the major product when a solution of pentafluorophenyl-lithium in ether decomposed in the presence of an excess of *NN*-dimethyl-*p*-toluidine. When the tetrafluorobenzene was generated from the Grignard reagent no products derived from the betaine (16) or the ylide (17) were detected. This is most probably due to the betaine (16) forming a complex with magnesium salts. The formation of similar complexes has been suggested.²³ We found that when pentafluorophenyl-lithium decomposed in ether in the presence of *NN*-dimethylaniline and magnesium bromide, neither of the products (15) and (18) was observed.

EXPERIMENTAL

Reactions involving Grignard reagents and organolithium compounds were carried out under dry, oxygen-free nitrogen, in apparatus dried overnight at 120°. Solvents were dried by conventional methods and solutions of products were dried over anhydrous magnesium sulphate. Analytical t.l.c. was carried out using silica gel (Merck GF₂₅₄) for layers 0.25 mm thick, and preparative layer chromatography (p.l.c.) was carried out using silica gel (Merck PF₂₅₄) for layers 0.75 mm thick. Analytical g.l.c. was carried out using a Pye 104 series chromatograph (5 ft column of 10% SE 30 on firebrick; flame ionisation detection).

I.r. spectra were determined for potassium bromide discs (solids) or thin films (liquids) using a Perkin-Elmer 257 spectrophotometer. U.v. spectra were determined using Unicam SP 800 or SP 8000 spectrophotometers. N.m.r. spectra were determined using a Perkin-Elmer R10 spectrometer at 60 (for ¹H) or 56.458 MHz (for ¹⁹F), with tetramethylsilane or trichlorofluoromethane as internal standard for ca. 20% w/v solutions. 100 MHz ¹H N.m.r. spectra were determined by the P.C.M.U. (Harwell) by courtesy of the S.R.C. ¹³C N.m.r. spectra at 25.2 MHz were determined by Dr. M. E. A. Cudby at I.C.I. Ltd., Plastics Division. Mass spectra were determined at 70 eV on an A.E.I. MS 12 spectrometer.

Light petroleum refers to the fraction of boiling range 60–80° unless otherwise specified.

Reactions of NN-Dimethylaniline with Tetrafluorobenzene.—*n*-Butyl-lithium (50 ml; 2.35M-solution in hexane) was added to bromopentafluorobenzene (24.7 g, 0.1 mol) in ether (150 ml) at –50°. The mixture was stirred at –50° for 15 min, and *NN*-dimethylaniline (70 ml) was added before the external cooling bath was removed. The mixture was stirred and allowed to warm to room temperature during 18 h. Water (250 ml) was added and the organic phase was dried and distilled, finally under vacuum, to remove the solvents and the excess of *NN*-dimethylaniline. The residual oil was taken into ether (100 ml) and extracted successively with (i) *N*-hydrochloric acid (3 × 25 ml), (ii) 2*N*-hydrochloric acid (4 × 25 ml), and (iii) 30% hydrochloric acid (5 × 25 ml). The three solutions were each neutralised with solid sodium carbonate and extracted with ether. Four fractions were thus obtained and a g.l.c. comparison of each with the crude oil showed that all were substantially homo-

geneous. The ratio of the four products in the crude mixture was 12 : 7 : 8 : 2.

Removal of the ether from fraction (i) gave 1-dimethylamino-5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene (1) (4.91 g, 18%), m.p. 83° (from ethanol) (Found: C, 62.4; H, 4.2; F, 28.2; N, 5.3%; *M*⁺ 269. C₁₄H₁₁F₄N requires C, 62.5; H, 4.1; F, 28.25; N, 5.2%; *M*, 269); τ (CCl₄) 2.9–3.4 (4H, m), 4.75–5.05 (1H, m), and 7.31 (6H, d, |*J*|_{HF} 5 Hz); ν_{max} (KBr) 2980, 2900, 2870, 2830, 1640, 1490, 1345, 1270, 1105, and 1050 cm⁻¹; λ_{max} (MeOH) 219 (ε 3880) and 265 nm (510).

Removal of the ether from fraction (ii) and elution through a short column of alumina gave 5-dimethylamino-1,2,3,4-tetrafluorobenzocyclo-octene (5) (2.68 g, 10%), b.p. 118° at 3 mmHg (satisfactory elemental analyses could not be obtained owing to rapid polymerisation); τ (CCl₄) 3.4–4.6 (4H, m), 5.21 (1H, d, |*J*| 3.0 Hz), and 7.47 (6H, s); ν_{max} 3020, 2960, 2850, 2810, 1650, 1520, 1470, 1355, 1155, 1140, and 1080 cm⁻¹; λ_{max} (cyclohexane) 217 (ε 11,870) and 263 nm (7000); *M*⁺ 269.

Removal of the ether from fraction (iii) gave *N*-methyl-*N*-2,3,4,5-tetrafluorobenzylaniline (15) (3.4 g, 13%), b.p. 115° at 2 mmHg (Found: C, 62.45; H, 4.25; N, 5.1%; *M*⁺ 269); τ (CDCl₃) 2.65–3.5 (6H, m), 5.55br (2H, s); and 7.05 (3H, s).

Removal of the ether from the residue of the original solution gave 5,6,7,8-tetrafluoro-3,4-dihydro-1,4-ethenonaphthalen-2(1*H*)-one (3) (1.7 g, 7%), m.p. 72–73° (after sublimation) (lit.,²⁴ 72.5–73.5°).

A repetition of the above reaction in which an ethereal solution of pentafluorophenyl-lithium was added to a solution of *NN*-dimethylaniline in hexane which was being heated under reflux gave the same compounds in the ratio 12 : 15 : 8 : 4 (g.l.c.).

When the first reaction was repeated with the addition of magnesium bromide (1 mol. equiv.) the ratio of the products was 24 : 5 : 0 : 6.

The first experiment was repeated except that light petroleum was substituted for the ether. Five products were isolated and shown to be compounds (1) (9.5%), (5) (2%), (15) (0.5%), and (3) (10%), and *N*-methyl-*N*-phenyltetrafluoro-*o*-toluidine (18) (19%) (Found: C, 62.4; H, 3.85; F, 28.1; N, 5.2%; *M*⁺ 269); τ (CDCl₃) 2.70–3.60 (5H, m), 6.83 (3H, s), and 7.95 (3H, dd, |*J*|_{HF} 2.4 and 1.2 Hz); ¹⁹F δ –142.5 (1F, m), –147.0 (1F, m), and –159.9 (2F, m).

When a solution of pentafluorophenylmagnesium bromide was heated in cyclohexane containing *NN*-dimethylaniline, compounds (1), (5), and (3) were isolated in 10, 1.5, and 0.75% yields, respectively.

*Reactions of Tetrafluorobenzene with NN-Dimethyl-*p*-toluidine.*—(i) *From pentafluorophenyl-lithium* [experiment by Dr. B. HANKINSON]. An identical work-up procedure gave (a) 1-dimethylamino-5,6,7,8-tetrafluoro-1,4-dihydro-4-methyl-1,4-ethenonaphthalene (7%), m.p. 49–50° (from light petroleum) (Found: C, 64.0; H, 4.85; N, 4.9%; *M*⁺ 283. C₁₅H₁₃F₄N requires C, 63.6; H, 4.6; N, 4.95%; *M*, 283); τ (CCl₄) 3.1 (2H, d, |*J*| 7 Hz), 3.58 (2H, d, |*J*| 7 Hz), 7.38 (6H, d, |*J*|_{HF} 4.5 Hz), and 7.97 (3H, d, |*J*|_{HF} 6 Hz); (b) 5-dimethylamino-1,2,3,4-tetrafluoro-8-methylbenzocyclo-octene (4%), an unstable oil; τ (CDCl₃) 3.4–4.6 (3H, m), 5.1 (1H, m), 7.47 (6H, s), and 8.3br (3H, s); (c) *N*-methyl-*N*-2,3,4,5-tetrafluorobenzyl-*p*-toluidine (12%), an oil (Found: C, 63.7; H, 4.9; N, 4.8%; *M*⁺, 283); τ (CCl₄) 3.18 (4H, AA'BB', |*J*|_{AB} 9.0 Hz), 3.2–3.5 (1H, m), 5.53br (2H, s), 7.05 (3H, s),

²³ G. Wittig and E. Benz, *Chem. Ber.*, 1959, **92**, 1999; H. Hellman and W. Unsel, *Annalen*, 1960, **631**, 82.

²⁴ I. F. Mikailova and V. A. Barkhash, *J. Org. Chem. (U.S.S.R.)*, 1970, **6**, 2335.

and 7.79 (3H, s); m/e 163 (60%, $C_7H_3F_4^+$); (d) *N*-methyl-*N*-*p*-tolyltetrafluoro-*o*-toluidine (29%), an oil (Found: C, 63.9; H, 4.7; N, 5.05%; M^+ , 283); τ (CCl_4) 3.30 (4H, AA'BB', $|J|_{AB}$ 8.4 Hz), 6.82 (3H, s), 7.78 (3H, s), and 7.93 (3H, d, $|J|_{HF}$ 3 Hz); and (e) 5,6,7,8-tetrafluoro-3,4-dihydro-9-methyl-1,4-ethenonaphthalen-2(1*H*)-one (9%), m.p. 78–80° (identical with an authentic sample¹).

(ii) From pentafluorophenylmagnesium bromide. This gave (a) 4%; (b) (3%), and (e) 4%.

Reaction of Tetrachlorobenzene with NN-Dimethylaniline.—When pentachlorophenyl-lithium was used this gave 5,6,7,8-tetrachloro-1-dimethylamino-1,4-dihydro-1,4-ethenonaphthalene (31%), m.p. 110° (from ethanol) (Found: C, 50.2; H, 3.3; N, 4.25%; M^+ , 335. $C_{14}H_{11}Cl_4N$ requires C, 50.3; H, 3.3; N, 4.2%; M , 335); τ (CCl_4) 2.9–3.3 (octet, AB of ABX, $|J|_{AB}$ 7, $|J|_{BX}$ 5.5, $|J|_{AX}$ 2 Hz), 4.55–4.85 (q, X of ABX), and 7.36 (6H, s); and 5-dimethylamino-1,2,3,4-tetrachlorobenzocyclo-octene (7) (4%), an unstable oil, τ (CCl_4) 3.3–4.5 (4H, m), 5.32 (1H, d, $|J|$ 3.2 Hz), and 7.48 (6H, s).

Photoisomerisation of 1-Dimethylamino-5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene.—Compound (1) (2.0 g) in light petroleum was irradiated with a 450 W Hanovia medium-pressure source under dry nitrogen for 100 h. After removal of the solvent the dark residue (765 mg) was eluted through a short column of alumina and subjected to p.l.c. to give (a) unchanged starting material (592 mg, 30%), (b) compound (5) (120 mg, 6%), identical with that already described (¹H n.m.r., i.r., and u.v. spectroscopy), and (c) 7-dimethylamino-9,10,11,12-tetrafluorotetracyclo-[6.4.0.0.2,4.0^{3,7}]dodeca-5,8,10,12-tetraene (9) (40 mg, 2%), an unstable oil, τ (CCl_4) 4.25 (1H, d, $|J|_{6,5}$ 5.0 Hz), 4.85 (1H, dd, $|J|_{5,6}$ 5.0, $|J|_{5,4}$ 2.0 Hz), 6.65 (2H, d, $|J|_{3,4}$ 6.5, $|J|_{2,4}$ 6.5 Hz), 7.05 (1H, dt, $|J|_{4,5}$ 2.0, $|J|_{4,2} = |J|_{4,3} = 6.5$ Hz), and 7.75 (6H, s).

Hydrogenations of Benzocyclo-octenes.—Compound (5) (700 mg) in ethanol (40 ml) was reduced slowly with hydrogen over pre-reduced palladium-carbon (70 mg; 10%) (uptake 2 mol. equiv.). Removal of the catalyst and solvent left a residue which, after p.l.c. [1 : 9 v/v ether-light petroleum (b.p. 40–60°)] gave 10-dimethylamino-1,2,3,4-tetrafluoro-5,6,7,8-tetrahydrobenzocyclo-octene (6) (428 mg, 61%), m.p. 62–63° (from hexane) (Found: C, 61.55; H, 5.5; N, 5.25%; M^+ , 273. $C_{14}H_{15}F_4N$ requires C, 61.55; H, 5.55; N, 5.15%; M , 273), τ (CCl_4) 5.24 (1H, t, $|J|$ 8 Hz), 7.47 (6H, s), and 6.8–9.0 (8H, m); ν_{max} . 3000, 2940, 2862, 2800, 1633, 1512, 1470, 1177, 1128, 1050, 943, and 821 cm^{-1} ; λ_{max} . (cyclohexane) 212 (ϵ 17,700) and 275 nm (2200).

Similarly, 5-dimethylamino-1,2,3,4-tetrafluoro-8-methylbenzocyclo-octene gave 10-dimethylamino-1,2,3,4-tetrafluoro-5,6,7,8-tetrahydro-7-methylbenzocyclo-octene (13), an oil, b.p. 94° at 0.25 mmHg (77%) (Found: C, 62.6; H, 6.25; N, 4.65%; M^+ , 287. $C_{15}H_{17}F_4N$ requires C, 62.7; H, 6.0; N, 4.9%; M , 287), τ (CCl_4) 5.25 (1H, t, $|J|$ 8.5 Hz), 7.49 (6H, s), 6.7–9.0 (7H, m), and 9.16 (3H, d, $|J|$ 5 Hz).

Similarly, compound (7) gave 1,2,3,4-tetrachloro-10-dimethylamino-5,6,7,8-tetrahydrobenzocyclo-octene (8) (70%), m.p. 81–82° (from ethanol) (Found: C, 49.65; H, 4.45; N, 4.1. $C_{14}H_{15}Cl_4N$ requires C, 49.6; H, 4.45; N, 4.15%); τ (CCl_4) 5.3 (1H, t, $|J|$ 7 Hz), 7.44 (6H, s), and 6.8–9.0 (8H, m).

Hydrolyses of 10-Dimethylamino-5,6,7,8-tetrahydrobenzocyclo-octenes.—Compound (6) (100 mg) was dissolved in

ethanol (5 ml; 10%) and hydrochloric acid (2 drops) and heated under reflux for 6 h. (The reaction was followed by g.l.c.). Evaporation of the solvents under reduced pressure gave 1,2,3,4-tetrafluoro-7,8,9,10-tetrahydrobenzocyclo-octen-5(6H)-one (11) (90 mg, 100%), b.p. 72° at 0.3 mmHg (Found: C, 58.4; H, 4.15%; M^+ , 246. $C_{12}H_{10}F_4O$ requires C, 58.55; H, 4.1%; M , 246), τ ($CDCl_3$) 7.1–7.5 (4H, m) and 8.0–8.5 (6H, m); ν_{max} . 2940, 2875, 1710, 1515, 1480, 1125, 1050, 935, and 875 cm^{-1} ; λ_{max} . (cyclohexane) 264 nm (ϵ 660).

The ketone (11) (68 mg) in dioxan (2 ml), deuterium oxide (1 ml), and sodium methoxide (5 mg) was heated under reflux for 50 h. Conventional work-up gave the 6,6-dideuterio-derivative (85%), τ ($CDCl_3$) 7.1–7.5 (2H, m) and 8.0–8.5 (6H, m); M^+ , 248 (88.5%) and 247 (11.5%).

Similarly compound (13) gave, after 48 h, 1,2,3,4-tetrafluoro-7,8,9,10-tetrahydro-8-methylbenzocyclo-octen-5(6H)-one (14) (88%), an oil (Found: C, 60.1; H, 4.6%; M^+ , 260. $C_{13}H_{12}F_4O$ requires C, 60.0; H, 4.65%; M , 260); τ (CCl_4) 7.0–7.5 (4H, m), 7.8–8.9 (5H, m), and 9.0 (3H, d, $|J|$ 6 Hz); ν_{max} . 1713 cm^{-1} .

Reduction of Compound (6).²⁵—Sodium borohydride (500 mg) was added to a solution of compound (6) (200 mg) in tetrahydrofuran (10 ml) under nitrogen. Glacial acetic acid (6 ml) was added dropwise to the stirred solution during 25 min, and the mixture was then heated under reflux for 1 h and cooled. Sodium hydroxide (20 ml; 20%) was added, and the solution was extracted with ether (4 × 10 ml). The extracts were washed with saturated aqueous sodium chloride, combined, dried, and evaporated to give 5-dimethylamino-1,2,3,4-tetrafluoro-5,6,7,8,9,10-hexahydrobenzocyclo-octene (12) (197 mg, 98%), m.p. 38.5° (after sublimation) (Found: C, 62.4; H, 6.25; N, 5.15. $C_{14}H_{17}F_4N$ requires C, 62.55; H, 6.2; N, 5.1%), τ ($CDCl_3$) 5.9–6.4 (2H, m), 7.0–7.4 (1H, m), 7.83 (6H, s), and 7.8–8.8 (8H, m).

Reaction of Tetrafluorobenzene with NN-Dimethylcyclohex-1-enylamine.—*n*-Butyl-lithium (10 ml; 0.02 mol solution in hexane was added to a solution of bromopentafluorobenzene (5 g, 0.02 mol) in ether (30 ml) at –70° and the mixture was stirred for 0.5 h. The amine (prepared in 59% yield²⁶) (0.5 g, 0.06 mol) was added, the external cooling source was removed, and the mixture was allowed to warm to room temperature. The mixture was then heated under reflux for 5 h, cooled, and diluted with ether (50 ml). Water (100 ml) was then added and the ethereal layer was extracted with hydrochloric acid (2*N*; 4 × 25 ml). The combined extracts were immediately neutralised with solid sodium carbonate and re-extracted with ether. The ethereal extract was dried and evaporated to leave an oil, which was eluted through a short column of alumina and gave 4a-dimethylamino-5,6,7,8-tetrafluoro-1,2,3,4,4a,8b-hexahydrobiphenylene (10) (2.5 g, 46%), b.p. 112° at 3 mmHg (Found: C, 61.35; H, 5.5; N, 4.85%; M^+ , 273. $C_{14}H_{15}F_4N$ requires C, 61.55; H, 5.55; N, 5.15%; M , 273), τ (CCl_4) 6.25–6.5 (1H, m), 7.69 (6H, s), 7.7–8.2 (4H, m), and 8.2–8.9 (4H, m), ν_{max} . 2938, 2880, 2849, 2800, 1635, 1500, 1280, 1031, and 897 cm^{-1} .

Removal of the ether and cyclohexanone from the non-basic fraction gave an oil which, after chromatography on a column of alumina, gave 2-(2,3,4,5-tetrafluorophenyl)cyclohexanone (300 mg, 6%), m.p. 95° (from ethanol) (Found: C, 59.05; H, 4.1%; M^+ , 246. $C_{12}H_{10}F_4O$ requires C, 58.5; H, 4.1%; M , 246), τ (CCl_4) 3.0–3.5 (1H, m), 6.0–6.5 (1H,

²⁵ J. A. Marshall and W. S. Johnson, *J. Org. Chem.*, 1963, **28**, 423.

²⁶ W. A. White and H. Weingarten, *J. Org. Chem.*, 1967, **32**, 213.

m), and 7.4—8.5 (8H, m), ν_{\max} 1710 cm^{-1} , λ_{\max} (EtOH) 261 nm (ϵ 960).

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