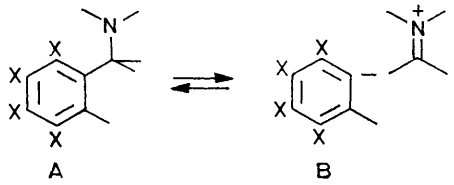
Rearrangement Reactions of Bicyclic Systems. Part II.[1] Rearrangements of 1-Dimethylamino-5,6,7,8-tetrahalogeno-1,4-dihydro-1,4-ethenonaphthalene Derivatives and the Analogous 5,6,7,8-Tetrafluoro-1,4-dihydro-*N*-methyl-1,4-iminonaphthalene in Aqueous Solutions

By **Harry Heaney** * and **Steven V. Ley**, Department of Chemistry, The University of Technology, Loughborough, Leicestershire LE11 3TU

The title compounds rearrange to biaryl derivatives in high yields in protic media. The isolation of ketonic derivatives when aromatisation is blocked shows that the driving force for the rearrangement is not provided predominantly by the aromatisation step. Evidence for an ionic mechanism is adduced from deuterium-incorporation studies.

We have shown previously [2] that an equilibrium exists between the structural features A and B (Scheme 1) which are present in the benzocyclobutene derivatives derived from the reactions of tetrahalogenobenzynes



A B

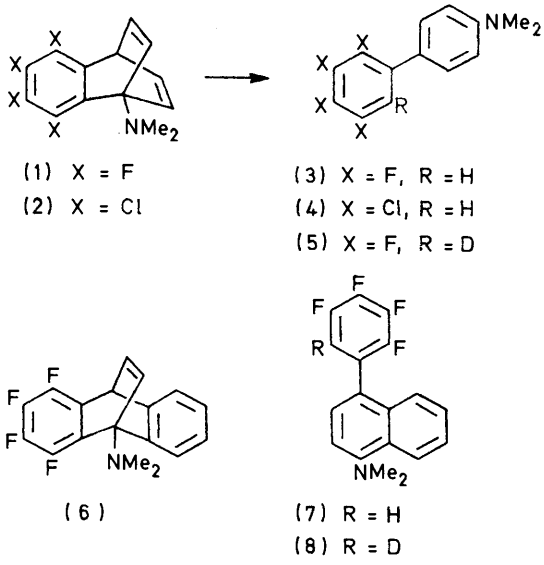
X = F or Cl

SCHEME 1

with enamines. Thus in protic media 2-arylcycloalkanones could be obtained in good yield. The same structural feature (in A) is also present in the benzobarrelenes (1,4-dihydro-1,4-ethenonaphthalenes) formed by the reactions of tetrahalogenobenzynes with *NN*-dimethylarylamines [3] and in 5,6,7,8-tetrahalogeno-1,4-dihydro-*N*-methyl-1,4-iminonaphthalenes.[4] In these compounds there are different geometrical arrangements of the *N*-*C*-aryl residues.

We now report the full details of our studies in this area.[5] When the benzobarrelene derivatives (1) and (2) were heated in aqueous ethanol they were slowly converted into the isomeric biphenyl derivatives (3) and (4), respectively. The formation of biaryl derivatives from benzobarrelene derivatives has few precedents.[6] The structures of compounds (3) and (4) followed from elemental analytical and spectral data. That the isomerisation does not proceed by an intramolecular process was shown by carrying out a reaction of compound (1) in 1,2-dimethoxyethane in the presence of deuterium oxide. Compound (5) was obtained, and shown by mass spectrometry to contain >99% ^{2}H. The position of the deuterium atom followed from the absence of the multiplet which was present in the ^{1}H n.m.r. spectrum of compound (3) at τ 2·8—3·3. In a control reaction we showed that compound (3) did not incorporate any deuterium under identical conditions.

In order to demonstrate the directing ability of the tetrahalogenoaryl system we prepared the dibenzobarrelene (6) by the reaction of tetrafluorobenzyne with *NN*-dimethyl-1-naphthylamine. When compound (6) was heated in aqueous diethylene glycol dimethyl ether at 140° we obtained only one product (7). The majority of the spectral data for this compound did not allow us to distinguish its structure from that of the alternative isomer. Thus, for example the single hydrogen atom on the tetrafluorophenyl group was not distinguishable from the naphthalenic protons in the ^{1}H n.m.r. spectrum. The mass spectrum was similarly uninformative: ions at *m/e* 149 and 77 were both present at low abundance (<4% of M^+). The most convincing evidence in favour of structure (7) was obtained from a comparison of its ^{19}F n.m.r. spectrum with that of the monodeuterio-derivative (8). The presence of ^{19}F,^{1}H spin–spin coupling was evident in the ^{19}F n.m.r. spectrum of



(1) X = F
(2) X = Cl
(3) X = F, R = H
(4) X = Cl, R = H
(5) X = F, R = D
(6)
(7) R = H
(8) R = D

SCHEME 2

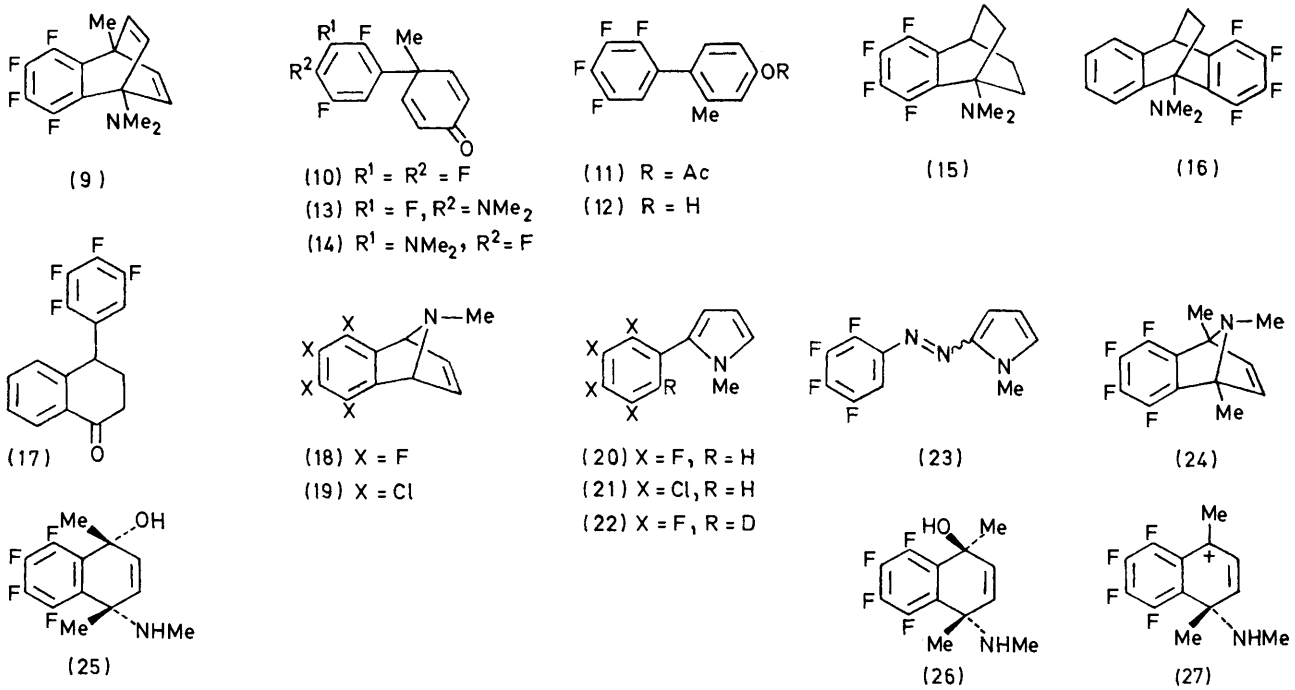
compound (7), whereas the spectrum of the compound (8) was much simpler because of the smaller J(^{19}F,^{2}H) values.

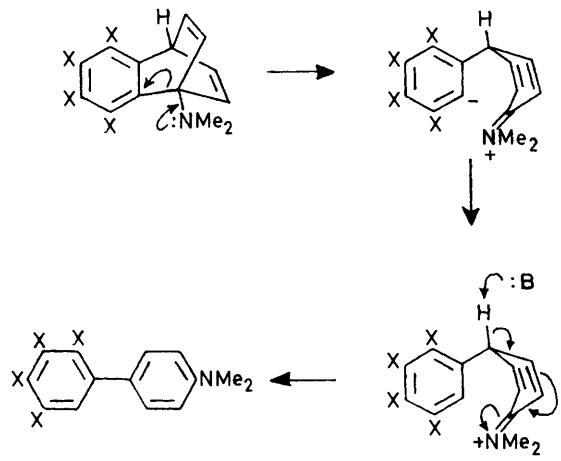
[1] Part I, H. Heaney, J. H. Hollinshead, G. W. Kirby, S. V. Ley, R. P. Sharma, and K. W. Bentley, *J.C.S. Perkin I*, 1973, 1840.
[2] H. Heaney and S. V. Ley, preceding paper.
[3] J. P. N. Brewer, H. Heaney, S. V. Ley, and T. J. Ward, *J.C.S. Perkin I*, 1974, 2688.
[4] D. D. Callander, P. L. Coe, J. C. Tatlow, and A. J. Uff, *Tetrahedon*, 1969, **25**, 25.
[5] H. Heaney and S. V. Ley, *Chem. Comm.*, 1970, 1184.
[6] See for example D. L. Fields and T. H. Regan, *J. Org. Chem.*, 1970, **35**, 1870.

We also wished to determine whether the driving force for the rearrangement was provided by the aromatisation step. We found that when compound (9) was heated in a sealed tube in aqueous diethylene glycol dimethyl ether at 140° the dienone (10) could be isolated in 25% yield. The spectral data for compound (10) compare well with those for the unhalogenated analogue.[7] The dienone (10) underwent the dienone–phenol rearrangement to the acetate (11) on treatment with perchloric acid in acetic anhydride, and the latter, (11), was converted into the phenol (12) with base. The migration of the methyl group is not unexpected in view of the presence of electron-withdrawing substituents on the aryl residue. We also obtained a 39% yield of an inseparable mixture of the dienones (13) and (14) from the hydrolysis of the amine (9). Since the reaction of compound (9) was carried out in a sealed tube it is not surprising that some replacement of fluoride ion by the dimethylamino-group should take place. The orientation of the substitution is in accord with other results of reactions with highly fluorinated arenes.[8]

If the rearrangement reactions of the 1-dimethylaminobenzobarrelene derivatives were governed only by the presence of the fragment A (Scheme 1), the fully reduced compound (15) would be expected to undergo rearrangement and hydrolysis to a 4-arylcyclohexanone. Attempts to bring about this conversion have failed. On the other hand we found that the dihydrodibenzobarrelene (16) can be converted slowly into the α-tetralone (17) by treatment with aqueous glycerol at 190° for 127 h.

A mechanism which accounts for these reactions is shown in Scheme 3. We prefer an ionic mechanism rather than a diradical process mainly as a result of the high level of deuterium incorporation obtained in the conversion (1) ⟶ (5). We would have expected that a diradical process would have resulted in hydrogen abstraction from the solvent, 1,2-dimethoxyethane. Some evidence for the intermediacy of a dipolar species was obtained by heating compound (1) in 1,2-dimethoxyethane containing diethyl maleate. A substantial





SCHEME 3

[7] H. E. Zimmerman, *J. Amer. Chem. Soc.*, 1970, **92**, 2753.

[8] J. Burdon, *Tetrahedron*, 1965, **21**, 3373; J. Burdon and W. B. Hollyhead, *J. Chem. Soc.*, 1965, 6326; J. G. Allen, J. Burdon, and J. C. Tatlow, *ibid.*, p. 6329; J. Burdon, W. B. Hollyhead, and J. C. Tatlow, *ibid.*, p. 6336; R. D. Chambers, personal communication; R. D. Chambers, W. K. R. Musgrave, J. S. Waterhouse, D. L. H. Williams, J. Burdon, W. B. Hollyhead, and J. C. Tatlow, *J.C.S. Chem. Comm.*, 1974, 239.

isomerisation of the diethyl maleate to diethyl fumarate was observed. Although it is known that secondary amines cause such isomerisations, tertiary amines do not.[9] This was checked in our system by using the amine (15) in place of compound (1); no isomerisation of maleate to fumarate occurred.

During our study the isomerisation of compound (18) to 1-methyl-2-(2,3,4,5-tetrafluorophenyl)pyrrole (20) was reported to occur either in 1,2-dihydroxyethane or in benzene at 180°.[10] The authors preferred a radical mechanism but presented no definitive evidence; they were also unable to prepare the pyrrole (20) by an independent route. We found that compounds (18) and (19) gave the pyrroles (20) and (21) in *ca.* 80% yield when heated in aqueous ethanol or aqueous 1,2-dihydroxyethane under reflux. When we heated a solution of (18) under reflux in 1,2-dimethoxyethane containing deuterium oxide we obtained compound (22) in which the level of deuterium incorporation was >99%. We prepared a sample of the pyrrole (20) by aprotic diazotisation of 2,3,4,5-tetrafluoroaniline in the presence of *N*-methylpyrrole. Not surprisingly we also obtained a large amount of the azo-compound (23) from this reaction.

We were unable to obtain any useful results using the adduct (24) formed by the reaction of tetrafluorobenzyne with 1,2,5-trimethylpyrrole. Although the adduct was undoubtedly formed in reasonable yield it was extremely unstable and gave a mixture of the epimeric amino-alcohols (25) and (26) on aqueous acidic work-up. These latter two products clearly arise from the cation (27), and this provides some evidence in favour of the previously suggested mechanism [11] for the decomposition of an adduct formed by the reaction of benzyne with a 1,2,5-trisubstituted pyrrole.

EXPERIMENTAL

The general methods used are given in ref. 3.

Isomerisation of 1-*Dimethylamino*-5,6,7,8-*tetrafluoro*-1,4-*dihydro*-1,4-*ethenonaphthalene* (1).—Compound (1) [3] (400 mg) was heated under reflux in aqueous ethanol (10 ml; 75%) for 20 h and gave, after removal of the solvent and crystallisation, 4′-*dimethylamino*-2,3,4,5-*tetrafluorobiphenyl* (3) (339 mg, 85%), m.p. 122—123° (from aqueous ethanol) (Found: C, 62·35; H, 4·2; N, 5·3%; M^+, 269. $C_{14}H_{11}F_4N$ requires C, 62·45; H, 4·15; N, 5·2%; *M*, 269), τ (CCl_4) 2·75 (2H, m, $|J|_{AB}$ 9, $|J|_{A,F}$ 1 Hz), 2·8—3·3 (1H, m), 3·39 (2H, m, $|J|_{BA}$ 9 Hz), and 7·02 (6H, s), ^{19}F δ −150·8 (m, 5-F), −155·1 (m, 2-F), −167·2 (m, 3-F), and −171·5 (m, 4-F) ($|J|_{2,3}$ 22·6, $|J|_{3,4}$ 22·0, $|J|_{4,5}$ 22·5, $|J|_{5,H}$ 12·0, $|J|_{2,H}$ 8·0, $|J|_{2,4}$ 2·0, $|J|_{4,H}$ 7·8, $|J|_{3,5}$ 2·0, $|J|_{2,5}$ 12·0, and $|J|_{3,H}$ 2·2 Hz), $\lambda_{max.}$ (EtOH) 220 (ε 13,500) and 310 nm (24,050).

Compound (1) (250 mg) heated under reflux in 1,2-dimethoxyethane (10 ml) and deuterium oxide (5 ml) gave compound (5) (76%), τ (CCl_4) 2·74 (2H, m, $|J|_{AB}$ 9, $|J|_{A,F}$ 1 Hz), 3·39 (2H, m, $|J|_{BA}$ 9 Hz), and 7·02 (6H, s); ^{19}F δ −150·8 (m, 5-F), −155·1 (m, 2-F), −167·2 (m, 3-F), and −171·5 (m, 4-F) ($|J|_{2,3}$ 22·6, $|J|_{3,4}$ 22·0, $|J|_{4,5}$ 22·5, $|J|_{3,5}$ = $|J|_{2,4}$ = 2·0, and $|J|_{2,5}$ 12·0 Hz), M^+ 270 (99%) and 269 (1). Compound (3) treated similarly was recovered unchanged as indicated by ^1H n.m.r. and mass spectrometry.

Isomerisation of 5,6,7,8-*Tetrachloro*-1-*dimethylamino*-1,4-*dihydro*-1,4-*ethenonaphthalene* (2).—Similarly compound (2), when heated under reflux in aqueous ethanol for 24 h, gave 2,3,4,5-*tetrachloro*-4′-*dimethylaminobiphenyl* (4) (93%), m.p. 112° (from ethanol) (Found: C, 50·0; H, 3·25; N, 4·1%; M^+, 335. $C_{14}H_{11}Cl_4N$ requires C, 50·3; H, 3·3; N, 4·2%; *M*, 335), τ (CCl_4) 2·7 (1H, s), 2·83 (2H, m, $|J|_{AB}$ 9 Hz), 3·38 (2H, m, $|J|_{BA}$ 9 Hz), and 7·03 (6H, s), $\lambda_{max.}$ (EtOH) 218 (ε 32,600), 235 (19,400), and 323 nm (18,400).

9-*Dimethylamino*-1,2,3,4-*tetrafluoro*-9,10-*dihydro*-9,10-*ethenoanthracene* (6).—1-Dimethylaminonaphthalene (20 g) was added to a solution of pentafluorophenyl-lithium [from bromopentafluorobenzene (14·8 g) in ether–hexane (100 ml; 7 : 3)] at −70°. The external cooling bath was removed and the mixture was kept at room temperature for 18 h. The usual [3] work-up gave a basic fraction (8·26 g) and chromatography on alumina gave the *ethenoanthracene* (6) (5·68 g, 30%), m.p. 94—96° (from light petroleum) (Found: C, 67·9; H, 4·0; N, 4·5%; M^+, 319. $C_{18}H_{13}F_4N$ requires C, 67·7; H, 4·1; N, 4·4%; *M*, 319), τ (CCl_4) 2·3—2·6 (1H, m), 2·7—3·2 (5H, m), 4·5—4·8 (1H, m), and 7·1 (6H, d, $|J|_{H,F}$ 5·0 Hz).

Isomerisation of the Ethenoanthracene (6).—Compound (6) (200 mg) in diethylene glycol dimethyl ether (7·5 ml) and water (2·5 ml) was heated in a sealed tube at 140° for 36 h. Water (10 ml) was added and the mixture was extracted with ether and gave, after preparative layer chromatography, starting material (32 mg) and 1-*dimethylamino*-4-(2,3,4,5-*tetrafluorophenyl*)*naphthalene* (7) (101 mg, 60%), m.p. 85—86° (from ethanol) (Found: C, 67·65; H, 4·2; N, 4·45%; M^+, 319. $C_{18}H_{13}F_4N$ requires C, 67·7; H, 4·1; N, 4·4%; *M*, 319), τ (CCl_4) 1·7—19·5 (1H, m), 2·5—3·3 (6H, m), and 7·13 (6H, s), ^{19}F δ −149·3 (m, 2-F), −150·0 (m, 5-F), −166·1 (m, 3-F), and −168·0 (m, 4-F) ($|J|_{2,3}$ 22·2, $|J|_{3,4}$ 21·5, $|J|_{4,5}$ 22·0, $|J|_{5,H}$ 11·5, $|J|_{4,H}$ 8·0, $|J|_{2,H}$ 7·0, $|J|_{3,5}$ 2·0, $|J|_{3,H}$ 2·0, and $|J|_{2,5}$ 12·0 Hz), $\lambda_{max.}$ (MeOH) 219 (ε 36,500), 240 (13,700), 323 and nm (8200).

Similarly compound (6) gave compound (8) in the presence of deuterium oxide; τ (CCl_4) 1·7—2·0 (1H, m), 2·5—3·1 (5H, m), and 7·13 (6H, s), M^+ 320 (99%) and 319 (1); ^{19}F δ −149·3 (m, 2-F), −150·0 (m, F-5), −166·1 (m, 3-F), and −168·0 (m, 4-F) ($|J|_{2,3}$ 22·2, $|J|_{3,4}$ 21·5, $|J|_{4,5}$ 22·0, $|J|_{3,5}$ 2·0, $|J|_{2,4}$ 2·0, and $|J|_{2,5}$ 12·0 Hz).

Rearrangement of 1-*Dimethylamino*-5,6,7,8-*tetrafluoro*-1,4-*dihydro*-4-*methyl*-1,4-*ethenonaphthalene* (9).—Compound (9) (900 mg) in diethylene glycol dimethyl ether (15 ml) and water (5 ml) containing sodium hydroxide (10 mg) was heated at 140° for 60 h in a sealed tube. The products were separated by preparative layer chromatography and gave 4-*methyl*-4-(2,3,4,5-*tetrafluorophenyl*)*cyclohexa*-2,5-*dienone* (10) (201 mg, 25%), m.p. 92—93° (from hexane) (Found: C, 61·05; H, 3·05%; M^+, 256. $C_{13}H_8F_4O$ requires C, 60·95; H, 3·15%; *M*, 256), τ (CCl_4) 2·85—3·3 (1H, m), 3·12 (2H, d, $|J|_{AB}$ 10 Hz), 3·80 (2H, d, $|J|_{BA}$ 10 Hz), and 8·31 (3H, d, $|J|$ 1 Hz), $\nu_{max.}$ ($CHCl_3$) 1675 and 1635 cm^{-1}, $\lambda_{max.}$ (EtOH) 238 (ε 16,400) and 265 nm (3090); ^{19}F δ −145·2 (m, 2-F), −146·3 (m, 5-F), −166·8 (m, 3-F), and −177·6 (m, 4-F) ($|J|_{2,3}$ 21·3, $|J|_{3,4}$ 21·5, $|J|_{4,5}$ 22·0, $|J|_{5,H}$ 11, $|J|_{4,H}$ 7·5, $|J|_{3,5}$ 2·0, $|J|_{2,4}$ 3·5, $|J|_{2,5}$ 12·0, and

[9] G. P. Clemo and S. B. Graham, *J. Chem. Soc.*, 1930, 213.
[10] P. L. Coe and A. J. Uff, *Tetrahedron*, 1971, 4065.
[11] E. Wolthuis, D. V. Jagt, S. Mels, and A. De Boer, *J. Org. Chem.*, 1965, **30**, 190.

$|J|_{3,H}$ 2·0 Hz); and an inseparable mixture of the dienones (13) and (14) (344 mg, 38%) in the ratio 1·5 : 1·0; τ ($CDCl_3$) 3·0—3·5 (1H, m), 3·1 (2H, d, $|J|$ 10 Hz), 3·83 (2H, d, $|J|$ 10 Hz), 7·11 (6H, t, $|J|_{H,F}$ 1·5 Hz), and 8·33 (3H, d, $|J|$ 1·0 Hz); $\nu_{max.}$ 1673 and 1630 cm^{-1}, M^{+} 281, ^{19}F δ −128·7 (0·8F), −133·4 (1·2F), −150·2 (2F), −153·8 (1·2F), and −154·9 (0·8F).

The dienone (10) (50 mg) was dissolved in carbon tetrachloride (25 ml) at 0° and perchloric acid (4 drops; 60%) in acetic anhydride (1 ml) was added slowly. The mixture was stirred for 15 min and added to water (50 ml). Normal work-up and preparative layer chromatography gave the dienone (10) (10 mg) and *4'-acetoxy-2,3,4,5-tetrafluoro-2'-methylbiphenyl* (11) (39 mg, 93%), m.p. 71—73° (from ethanol) (Found: C, 60·65; H, 3·55%; M^{+}, 298. $C_{15}H_{10}F_4O_2$ requires C, 60·4; H, 3·4%; *M*, 298); τ (CCl_4) 2·7—3·4 (4H, m), 7·76 (3H, s), and 7·77br (3H, s), $\nu_{max.}$ 1760 cm^{-1}, $\lambda_{max.}$ (MeOH) 214 (ε 17,250), 236 (10,800), and 260 nm (2820).

The acetate (11) (20 mg) in aqueous ethanol (1 ml; 5%) containing sodium carbonate (5 mg) was stirred at room temperature for 3 h. Acidification and crystallisation gave *2,3,4,5-tetrafluoro-4'-hydroxy-2'-methylbiphenyl* (12) (14 mg, 82%), m.p. 105—106° (from ethanol) (Found: C, 61·25; H, 3·35. $C_{13}H_8F_4O$ requires C, 61·15; H, 3·15%); τ (CCl_4) 2·9—3·4 (4H, m), 5·44br (1H, s, exchangeable), and 7·89br (3H, s).

Reduction of Compound (6).—Compound (6) (500 mg) in ethanol (25 ml) was reduced with hydrogen at atmospheric pressure over palladium–carbon and gave *9-dimethylamino-1,2,3,4-tetrafluoro-9,10-dihydro-9,10-ethanoanthracene* (16) (500 mg, 99%), m.p. 100—101° (from ethanol) (Found: C, 67·2; H, 4·85; N, 4·35%; M^{+}, 321. $C_{18}H_{15}F_4N$ requires C, 67·3; H, 4·7; N, 4·35%; *M*, 321). τ (CCl_4) 2·3—2·6 (1H, m), 2·6—3·1 (3H, m), 5·38—5·55 (1H, m), 7·25 (6H, d, $|J|_{H,F}$ 7·0 Hz), and 8·0—8·6 (4H, m).

Similarly hydrogenation of compound (1) gave *1-dimethylamino-5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-1,4-ethanonaphthalene* (15) (90%), m.p. 76—78° (from ethanol) (Found: C, 61·5; H, 5·4; F, 27·5; N, 5·1%; M^{+}, 273. $C_{14}H_{15}F_4N$ requires C, 61·5; H, 5·5; F, 27·8; N, 5·1%; *M*, 273), τ (CCl_4) 6·5—6·7 (1H, m), 7·58 (6H, d, $|J|_{H,F}$ 5·0 Hz), and 8·0—8·9 (8H, m).

Hydrolysis of Compound (16).—Compound (16) (237 mg) in glycerol (7·5 ml) and water (2·5 ml) was heated in a sealed tube at 190° for 127 h. Normal work-up followed by preparative layer chromatography gave starting material (99 mg) and *3,4-dihydro-4-(2,3,4,5-tetrafluorophenyl)-naphthalen-1(2H)-one* (17) (16 mg, 13%), m.p. 95—96° (from ethanol) (Found: C, 65·5; H, 3·5%; M^{+}, 294. $C_{16}H_{10}F_4O$ requires C, 65·3; H, 3·45%; *M*, 294), τ (CCl_4) 1·85—2·15 (1H, m), 2·4—2·8 (2H, m), 2·9—3·2 (1H, m), 3·3—3·8 (1H, m), 5·38 (1H, t), $|J|$ 6 Hz), and 7·2—7·9 (4H, m), $\nu_{max.}$ 1690 cm^{-1}, $\lambda_{max.}$ (MeOH) 218 (ε 15,200), 246 (6850), and 291 nm (1230).

Isomerisation of 5,6,7,8-Tetrafluoro-1,4-dihydro-N-methyl-1,4-iminonaphthalene (18).—Compound (18) [4] (150 mg) was heated under reflux in ethylene glycol for 4 h. Conventional work-up gave 1-methyl-2-(2,3,4,5-tetrafluorophenyl)pyrrole (20) (110 mg, 73%), m.p. 25—26° (lit.,[10] 28—29°), identical with a sample prepared by an alternative method.

Compound (18) (200 mg) was heated under reflux for 18 h in diethylene glycol dimethyl ether (10 ml) containing deuterium oxide (1 ml). Conventional work-up gave the pyrrole (22) (110 mg, 55%), τ ($CDCl_3$) 3·3—3·4 (1H, m), 3·8—4·0 (2H, m), and 6·45 (3H, d, $|J|$ 1·5 Hz), M^{+} 230 (99%) and 229 (1). The undeuteriated pyrrole (20) did not undergo exchange in a control experiment.

Aprotic Diazotisation of 2,3,4,5-Tetrafluoroaniline in the Presence of N-Methylpyrrole.—2,3,4,5-Tetrafluoroaniline (830 mg), acetic anhydride (1·55 g), and *N*-methylpyrrole (6·5 g) were dissolved in carbon tetrachloride (50 ml) to which was then added pentyl nitrite (1·55 g). The mixture was heated under reflux for 1 h and stirred at room temperature for a further 3 h. The solvent and the excess of reagents were removed and the residue placed on a column of alumina. Elution with light petroleum gave the pyrrole (20) (14%), identified by t.l.c., g.l.c., and i.r. and n.m.r spectroscopy, followed by *1-methyl-2-(2,3,4,5-tetrafluorophenylazo)pyrrole* (23) (480 mg, 40%), m.p. 95—96° (yellow needles from hexane) (Found: C, 51·15; H, 2·9; N, 16·35%; M^{+}, 257. $C_{11}H_7F_4N_3$ requires C, 51·35; H, 2·75; N, 16·35%; *M*, 257); τ (CCl_4) 2·4—2·9 (1H, m), 3·0—3·15 (1H, m), 3·23 (1H, dd, $|J|_{2,3}$ 4·5, $|J|_{2,4}$ 1·0 Hz), 3·75 (1H, dd, $|J|_{3,2}$ 4·5, $|J|_{3,4}$ 3·0 Hz), and 6·06 (3H, s), $\lambda_{max.}$ (EtOH) 350 (ε 9000) and 398 nm (17,000).

Isomerisation of Compound (19).—Compound (19) [12] gave 1-methyl-2-(2,3,4,5-tetrachlorophenyl)pyrrole (21) (81%), m.p. 99—101° (after sublimation), τ ($CDCl_3$) 2·58 (1H, s), 3·25 (1H, m), 4·7—4·9 (2H, m), and 6·54 (3H, s), $\lambda_{max.}$ (EtOH) 210 (ε 37,600) and 305 nm (6400).

Reaction of Tetrafluorobenzyne with 1,2,5-Trimethylpyrrole.—By the method of ref. 4 the reaction gave a tarry product from which were obtained, by a combination of distillation under reduced pressure and preparative layer chromatography, compounds (*a*)—(*c*).

(*a*) 1,4-Dimethyl-5,6,7,8-tetrafluoro-1,4-dihydro-*N*-methyl-1,4-iminonaphthalene (24) (6%) had m.p. 54° (from hexane), τ ($CDCl_3$) 3·25 (2H, s), 7·96 (3H, s), and 8·23br (6H, s), M^{+} 257, and decomposed readily even at −20° under nitrogen.

(*b*) *5,6,7,8-Tetrafluoro-1,4-dihydro-4-methylamino-cis-1,4-dimethyl-1-naphthol* (25) (6%) had m.p. 156—158° (from methanol) (Found: C, 56·55; H, 4·75; N, 5·15%; M^{+}, 275. $C_{13}H_{13}F_4NO$ requires C, 56·75; H, 4·75; N, 5·1%; *M*, 275), τ ($CDCl_3$) 4·1 (1H, d, $|J|$ 4·5 Hz), 4·75 (1H, d, $|J|$ 4·5 Hz), 7·5br (2H, s, exchangeable), 8·11br (6H, s), and 8·4 (3H, d, $|J|$ 1 Hz), $\nu_{max.}$ 3600 cm^{-1}.

(*c*) 5,6,7,8-Tetrafluoro-1,4-dihydro-4-methylamino-*trans*-1,4-dimethyl-1-naphthol (26) (5%) had m.p. 123—127° (from hexane), M^{+} 275, τ ($CDCl_3$) 4·0—4·2 (1H, m), 4·7—4·9 (1H, m), 7·8—8·4 (2H, m, exchangeable), 8·0 (3H, s), 8·1 (3H, m), and 8·5 (3H, d, $|J|$ 1·5 Hz), $\nu_{max.}$ 3350 cm^{-1}.

We thank the S.R.C. for a studentship (to S. V. L.) and the Imperial Smelting Corporation (Avonmouth) for supplies of fluorinated starting materials.

[12] G. W. Gribble, N. R. Easton, jun., and J. T. Eaton, *Tetrahedron Letters*, 1970, 1075.

[4/1239 *Received*, 24*th June*, 1974]