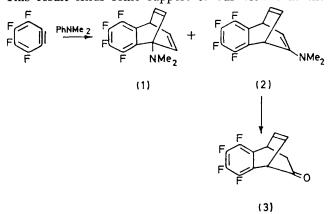
## Aryne Chemistry. Part XXXIV.<sup>1</sup> Reactions of NN-Dimethylarylamines with Tetrahalogenobenzynes

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Reactions of tetrafluorobenzyne with NN-dimethylarylamines lead to mixtures of products. When the aryne is generated from a Grignard reagent the isolated products are those derived from attack on the arene residue and have been characterised as derivatives of 1,4-dihydro-1,4-ethenonaphthalene and benzocyclo-octene. Two additional products identified in reactions with pentafluorophenyl-lithium are derived from a betaine either by immediate charge neutralisation or by ylide formation followed by a Stevens rearrangement in which aryl migration occurs.

We have shown that reactions of methoxyarenes with tetrahalogenobenzynes lead to good yields of 1,4-cycloadducts in which the predominant products are 1,4dihydro-1-methoxy-1,4-ethenonaphthalenes (1-methoxybenzobarrelenes).<sup>1</sup> We have now studied similar reactions of NN-dimethylarylamines in order to test the idea that electron-releasing substituents in an arene might in general lead to benzobarrelene derivatives functionalised at a bridgehead position.<sup>2</sup>

Reactions of benzyne with tertiary amines have been studied previously in considerable detail<sup>3</sup> but in these reactions, including for example those with NN-dimethylaniline,<sup>4</sup> the products arise exclusively from initial reaction at the nitrogen atom. When tetrafluorobenzyne was generated by the decomposition of pentafluorophenylmagnesium bromide at 80° in the presence of NN-dimethylaniline, three products were detected by g.l.c. The major product, isolated in 10% yield, was the 1,4-cycloadduct, 1-dimethylamino-5,6,7,8expected tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene (1), and the second product, isolated in 1% yield, was the ketone (3), evidently derived by hydrolysis of the enamine (2). This result lends some support to our view that the



## SCHEME 1

presence of electron-releasing substituents in arenes may result in the attainment of a transition state in which bond formation is more advanced at the para-position (4) and hence leads to bridgehead-functionalised benzobarrelenes. The third product, present in very low

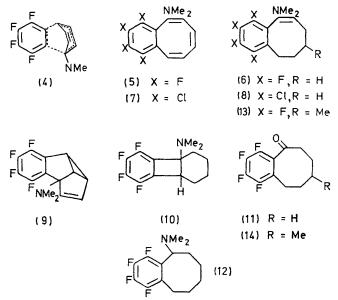
Part XXXIII, P. C. Buxton, N. J. Hales, B. Hankinson, H. Heaney, S. V. Ley, and R. P. Sharma, preceding paper.
 Preliminary account, H. Heaney and T. J. Ward, Chem.

Comm., 1969, 810. <sup>3</sup> R. W. Hoffmann, 'Dehydrobenzene and Cycloalkynes,'

Academic Press, New York, 1967.

yield, was so unstable that it was only isolated in reactions carried out with pentafluorophenyl-lithium.

When a solution of pentafluorophenyl-lithium was allowed to decompose at room temperature in ether containing an excess of NN-dimethylaniline, four products were detected by g.l.c. in the ratio (a) 12: (b) 3: (3) 7: (d) 8. The mixture was separated by extraction with aqueous hydrochloric acid of various concentrations; the isolated yields of the products were (a) 18%, (b) 7%, (c) 10%, and (d) 13%.



The products (a) and (b) were found to be the compounds (1) and (3), of which the latter has been reported previously.<sup>5</sup> The structure of compound (1) is evident from its analytical figures and spectral data. In particular the *peri*-relationship of the dimethylamino-group and a fluorine atom is shown by the presence of a doublet (|I| 5 Hz) in the <sup>1</sup>H n.m.r. spectrum at  $\tau$  7.31, due to long-range <sup>19</sup>F,H spin-spin coupling.<sup>6</sup> The third product (c) was originally thought to be a derivative of 4a,8bdihydrobiphenylene,<sup>2</sup> largely on the grounds of its failure to take up more than 2 mol. equiv. of hydrogen in the presence of palladium and its u.v. spectrum. This 4 A. R. Lepley, A. G. Giumanini, A. B. Giumanini, and W. A.

A. R. Lepley, A. G. Gumannin, A. B. Gumannin, and W. A. Khan, J. Org. Chem., 1966, **31**, 2051; A. R. Lepley, Amer. Chem. Soc., Div. Petrol. Chem., 1969, **14** (2), C43.
J. P. N. Brewer, I. F. Eckhard, H. Heaney, and B. A. Marples, J. Chem. Soc. (C), 1968, 664.
J. P. N. Brewer, H. Heaney, and B. A. Marples, Chem. Comm. 1967, 27

Comm., 1967, 27.

product was particularly difficult to characterise, owing to its instability. For example a sample was  $ca. 90\sqrt[6]{o}$ polymerised after 24 h under nitrogen at  $-25^{\circ}$ . No stable examples of 4a,8b-dihydrobiphenylenes appear to be known; <sup>7</sup> usually such compounds undergo valencebond isomerisation to the thermally more stable benzocyclo-octenes.<sup>8</sup> 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  $\lambda_{max}$  263 nm ( $\epsilon$  7000), the <sup>1</sup>H n.m.r. spectrum had resonances at  $\tau$ 3·38-4·5 (4H), 5·15 (1H), and 7·42 (6H), and the mass spectrum showed significant peaks at m/c 269, 254, 240, 225, and 224. The u.v. spectrum could be due to a benzocyclo-octene chromophore.<sup>8a</sup> Both compounds (5)and (6) showed strong peaks in their i.r. spectra at ca. 1650 cm<sup>-1</sup> which are characteristic of enamines.<sup>9</sup>

In the <sup>1</sup>H n.m.r. spectrum of compound (5) a quartet (1H) centred at  $\tau 3.53$  ([J] 12 and 1.5 Hz) is analogous to the doublet associated with the protons adjacent to the benzo-ring in benzocyclo-octene ( $\tau$  3·49; |1| 12 Hz).<sup>10</sup> The additional coupling (1.5 Hz) is presumably due to long-range <sup>19</sup>F,H interaction, since in the tetrachloroanalogue (7) we only observed a doublet at  $\tau 3.49$  (|] 12 Hz). Compound (5) and its tetrachloro-analogue (7) also showed broadened doublets in the <sup>1</sup>H n.m.r. spectra at  $\tau$  ca. 5.21 ([J] 3 Hz), in good accord with reported chemical shifts for enamine vinylic protons.9 NN-Dimethylcyclo-octatetraenylamine, reported recently,96 shows resonances at  $\tau 4.2$  (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 benzobarrelene (1), although this was expected <sup>11</sup> 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 benzosemibullvalene (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 dimethylaminobenzocyclobutene (10) was prepared by the reaction of tetrafluorobenzyne with NN-dimethylcyclohex-1-enylamine. The comparison showed that the compounds were not identical, and further that they could not be epimers. We originally reported <sup>2</sup> that the tetrahydroderivative (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,  $\lambda_{max}$  264 nm ( $\epsilon$  660),  $\nu_{max}$  1710 cm<sup>-1</sup> (C=O). Although this i.r. frequency is high for a normal aryl ketone<sup>12</sup> it is not unusual in polyfluoroaryl carbonyl compounds.<sup>13</sup> <sup>1</sup>H N.m.r. spectroscopy showed the presence of methylene groups adjacent to aryl and carbonyl residues  $[\tau 7.1 - 7.5 (4H)]$  and other methylene resonances at  $\tau 8.0-8.5$  (6H). The noise-decoupled <sup>13</sup>C n.m.r. spectrum showed resonances (downfield from Me<sub>4</sub>Si) 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 <sup>13</sup>C,<sup>19</sup>F coupling and to long relaxation times. These data are in accord with published values 14 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

<sup>&</sup>lt;sup>7</sup> 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.

<sup>&</sup>lt;sup>8</sup> (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.

<sup>&</sup>lt;sup>9</sup> (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. <sup>10</sup> J. A. Elix and M. V. Sargent, J. Amer. Chem. Soc., 1969, **91**,

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<sup>&</sup>lt;sup>11</sup> 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.,

<sup>Zimmerman, R. S. Givens, and R. M. Pagni, J. Amer. Chem. Soc., 1968, 90, 6096.
<sup>12</sup> L. J. Bellamy, 'The Infra-red Spectra of Complex Molecules,' Methuen, London, 1958, p. 132.
<sup>13</sup> 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.
<sup>14</sup> 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-</sup>

Nuclear Magnetic Resonance for Organic Chemists,' Wiley-Interscience, New York, 1972.

<sup>&</sup>lt;sup>15</sup> J. Sato, K. Murata, and A. Nichimura, Tetrahedron, 1967, 23. 1791.

obtained in reactions of tetrafluorobenzyne with NNdimethyl-p-toluidine and of tetrachlorobenzyne with NNdimethylaniline. Both these compounds were hydrogenated, to give, respectively, the enamines (13) and (8), and the former compound was hydrolysed to the ketone (14).

The benzocyclo-octene derivatives must be formed by valence-bond isomerisation of initial 1,2-cycloadducts. The ring opening of *cis*-fused 4a,8b-dihydrobiphenylenes can occur under orbital symmetry control by disrotation. The epimeric *trans*-fused 4a,8b-dihydrobiphenylenes would be expected to be much more stable since a disrotatory ring opening would lead to a *trans*-double bond in the cyclo-octene ring. The alternative conrotatory ring opening would occur *via* an *o*-quinodimethane transition state. It is therefore unlikely that the initial formation of the 1,2-cycloadducts between arynes and *NN*-dimethylarylamines occurs by a concerted mechanism. A concerted mechanism would require a  $[\pi 2s + \pi 2a]$  cycloaddition and this would produce a *trans*-4a,8b-dihydrobiphenylene.

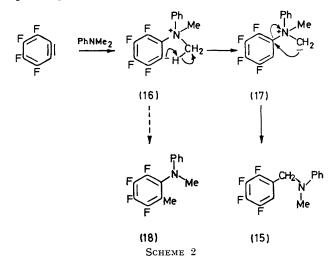
The fourth product from the reaction of tetrafluorobenzyne with NN-dimethylaniline in which the aryne was generated from pentafluorophenyl-lithium in ether was less basic than the other two basic products (1) and (5), with which it was isomeric, and was shown to be Nmethyl-N-2,3,4,5-tetrafluorobenzylaniline (15). The <sup>1</sup>H n.m.r. and i.r. spectral data are fully in accord with this structure, and any ambiguity was completely removed by the mass spectrum. Structurally significant ions were observed at m/e 269 (100%,  $M^{\ddagger}$ ), 163 (55,  $C_7H_3F_4^+$ ), 120 (86,  $C_8H_{10}N^+$ ), 106 (63,  $C_7H_8N^+$ ), and 77 (77,  $C_6H_5^+$ ). In particular the observation of the ion at m/e 163, which corresponds to the tetrafluorotropylium ion, and the complete absence of an ion at m/e 91 confirmed the structure.

The amine (15) corresponds to the product of an unusual Stevens rearrangement. In addition, no products derived from attack at nitrogen were observed in our reactions carried out with pentafluorophenylmagnesium bromide. No verified examples of Stevens rearrangements <sup>16</sup> involving a migration of an aryl residue had been reported prior to our preliminary communication. Migration of a naphthyl residue has been reported subsequently.<sup>17</sup> Our results suggest that the initial product is the betaine (16); this is then converted to the ylide (17), which undergoes a Stevens rearrangement to the product (15). The possibility that the product arises by the addition of a metallated derivative of NN-dimethylaniline is excluded by the fact that no deuterium incorporation was observed when the reaction mixture was quenched with deuterium oxide.

<sup>18</sup> T. S. Stevens, in 'Progress in Organic Chemistry,' vol. 7, eds. Sir James Cook and W. Carruthers, Butterworths, London, 1968.

<sup>17</sup> W. E. Truce and D. L. Heuring, *Chem. Comm.*, 1969, 1499.
 <sup>18</sup> T. S. Stevens, E. H. Creighton, A. B. Gordon, and M. Mc <sup>18</sup> Chem. Sci. 1980, 2129

Nicol, J. Chem. Soc., 1928, 3193. <sup>19</sup> T. S. Stevens, J. Chem. Soc., 1930, 2107; R. A. W. Johnstone and T. S. Stevens, *ibid.*, 1955, 4487; R. R. Hill and T.-H. Chan, J. Amer. Chem. Soc., 1966, **88**, 866. Although the Stevens rearrangement has been known for many years <sup>18</sup> and is regarded as an intramolecular process, <sup>19</sup> it is still the subject of considerable discussion.<sup>20</sup> Since we have no firm evidence we would only point out that the known ease of nucleophilic substitution in polyfluoroaryl systems <sup>21</sup> is in accord with a concerted process operating under orbital symmetry control.<sup>22</sup>



When pentafluorophenyl-lithium decomposed in light petroleum in the presence of NN-dimethylaniline, five products were obtained. Four of them were compounds (1), (3), (5), and (15) isolated in  $9 \cdot 5$ ,  $10 \cdot 0$ ,  $2 \cdot 0$ , and  $0 \cdot 5 \%$ yields, respectively. The fifth product, isolated in 19%yield, was isomeric with the other three bases and is assigned structure (18) (Scheme 2). This product must be formed as a result of the high tendency towards charge neutralisation in the betaine (16) in the solvent system of low polarity. Molecular models reveal that an intramolecular process would involve a front-side displacement of the methyl group; therefore an intermolecular process is more likely.

The reaction of tetrafluorobenzyne with NN-dimethylaniline in light petroleum, which affords the compound (18) as the major product, suggests that the betaine is not

<sup>20</sup> J. H. Brewster and M. W. Kline, J. Amer. Chem. Soc., 1952, 74, 5179; E. F. Jenny and J. Druey, Angew. Chem. Internat. Edn., 1962, 1, 155; U. Schöllkopf and W. Fabian, Annalen, 1961, 642, 1; D. J. Cram, 'Fundamentals of Carbanion Chemistry,' Academic Press, New York, 1965, p. 223; R. W. Jemison and D. G. Morris, Chem. Comm., 1969, 1226; A. R. Lepley, J. Amer. Chem. Soc., 1969, 91, 1237; Chem. Comm., 1969, 1460; U. Schöllkopf, W. Ludwig, G. Ostermann, and M. Patsch, Tetrahedron Letters, 1969, 3415; H. P. Benecke and J. H. Wikel, *ibid.*, 1971, 3479; A. R. Lepley and A. G. Giumanini, in 'Mechanisms of Molecular Migrations,' ed. B. S. Thyagarajan, Wiley-Interscience, New York, 1970; W. K. Musker, Fortschr. Chem. Forsch., 1970, 14, 295.

<sup>290.</sup>
<sup>21</sup> 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, *I.C.S. Chem. Comm.*, 1974, 239.

 J. C. Tatlow, J.C.S. Chem. Comm., 1974, 239.
 <sup>22</sup> R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Verlag Chemie, G.m.b.H., Weinheim, 1970, p. 131. 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 tetrafluorobenzyne 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.<sup>23</sup> 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 GF<sub>254</sub>) for layers 0·25 mm thick, and preparative layer chromatography (p.l.c.) was carried out using silica gel (Merck PF<sub>254</sub>) 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 <sup>1</sup>H) or 56.458 MHz (for <sup>19</sup>F), with tetramethylsilane or trichlorofluoromethane as internal standard for *ca.* 20% w/v solutions. 100 MHz <sup>1</sup>H N.m.r. spectra were determined by the P.C.M.U. (Harwell) by courtesy of the S.R.C. <sup>13</sup>C 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  $60-80^{\circ}$  unless otherwise specified.

Reactions of NN-Dimethylaniline with Tetrafluorobenzyne. -n-Butyl-lithium (50 ml; 2·35м-solution in hexane) was added to bromopentafluorobenzene (24.7 g, 0.1 mol) in ether (150 ml) at  $-50^{\circ}$ . The mixture was stirred at  $-50^{\circ}$  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 ( $3 \times 25$  ml), (ii) 2Nhydrochloric acid ( $4 \times 25$  ml), and (iii) 30% hydrochloric acid (5  $\times$  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-

<sup>23</sup> G. Wittig and E. Benz, *Chem. Ber.*, 1959, **92**, 1999; H. Hellman and W. Unseld, *Annlaen*, 1960, **631**, 82. 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%;  $M^{\ddagger}$  269. C<sub>14</sub>H<sub>11</sub>F<sub>4</sub>N requires C, 62·5; H, 4·1; F, 28·25; N, 5·2%; M, 269);  $\tau$  (CCl<sub>4</sub>) 2·9—3·4 (4H, m), 4·75—5·05 (1H, m), and 7·31 (6H, d,  $|J|_{\rm HF}$ 5 Hz);  $\nu_{\rm max}$  (KBr) 2980, 2900, 2870, 2830, 1640, 1490, 1345, 1270, 1105, and 1050 cm<sup>-1</sup>;  $\lambda_{\rm max}$  (MeOH) 219 ( $\varepsilon$  3880) and 265 nm (510).

Removal of the ether from fraction (ii) and elution through a short column of alumina gave 5-dimethylamino-1,2,3,4tetrafluorobenzocyclo-octene (5) (2.68 g, 10%), b.p. 118° at 3 mmHg (satisfactory elemental analyses could not be obtained owing to rapid polymerisation);  $\tau$  (CCl<sub>4</sub>) 3.4—4.6 (4H, m), 5.21 (1H, d, |f| 3.0 Hz), and 7.47 (6H, s);  $\nu_{max}$  3020, 2960, 2850, 2810, 1650, 1520, 1470, 1355, 1155, 1140, and 1080 cm<sup>-1</sup>;  $\lambda_{max}$  (cyclohexane) 217 ( $\varepsilon$  11,870) and 263 nm (7000);  $M^{\pm}$  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);  $\tau$  (CDCl<sub>3</sub>) 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-etheno-naphthalen-2(1H)-one (3) (1.7 g, 7%), m.p. 72—73° (after sublimation) (lit.,<sup>24</sup> 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%;  $M^{\pm}$ , 269);  $\tau$  (CDCl<sub>3</sub>) 2.70—3.60 (5H, m), 6.83 (3H, s), and 7.95 (3H, dd,  $|J|_{\rm HF}$  2.4 and 1.2 Hz); <sup>19</sup>F  $\delta$  – 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 Tetrafluorobenzyne with NN-Dimethyl-ptoluidine.—(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-4methyl-1,4-ethenonaphthalene (7%), m.p. 49—50° (from light petroleum) (Found: C, 64·0; H, 4·85; N, 4·95%; M, 283);  $\tau$  (CCl<sub>4</sub>) 3·1 (2H, d, |J| 7 Hz), 3·58 (2H, d, |J| 7 Hz), 7·38 (6H, d,  $|J|_{\rm HF}$  4·5 Hz), and 7·97 (3H, d,  $|J|_{\rm HF}$  6 Hz); (b) 5-dimethylamino-1,2,3,4-tetrafluoro-8-methylbenzocyclo-octene (4%), an unstable oil;  $\tau$  (CDCl<sub>3</sub>) 3·4—4·6 (3H, m), 5·1 (1H, m), 7·47 (6H, s), and 8·3br (3H, s); (c) N-methyl-N-2,3,4,5tetrafluorobenzyl-p-toluidine (12%), an oil (Found: C, 63·7; H, 4·9; N, 4·8%; M<sup>±</sup>, 283);  $\tau$  (CCl<sub>4</sub>) 3·18 (4H, AA'BB',  $|J|_{\rm AB}$  9·0 Hz), 3·2—3·5 (1H, m), 5·53br (2H, s), 7·05 (3H, s),

<sup>24</sup> 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-Np-tolyltetrafluoro-o-toluidine (29%), an oil (Found: C, 63.9; H, 4.7; N, 5.05%;  $M^{\ddagger}$ , 283);  $\tau$  (CCl<sub>4</sub>) 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-9methyl-1,4-ethenonaphthalen-2(1H)-one (9%), m.p. 78—80° (identical with an authentic sample <sup>1</sup>).

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

Reaction of Tetrachlorobenzyne with NN-Dimethylaniline. When pentachlorophenyl-lithium was used this gave 5,6,7,8tetrachloro-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<sup>+</sup>, 335. C<sub>14</sub>H<sub>11</sub>Cl<sub>4</sub>N requires C, 50·3; H, 3·3; N, 4·2%; M, 335);  $\tau$  (CCl<sub>4</sub>) 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-1,2,3,4tetrachlorobenzocyclo-octene (7) (4%), an unstable oil,  $\tau$ (CCl<sub>4</sub>) 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 (<sup>1</sup>H n.m.r., i.r., and u.v. spectroscopy), and (c) 7-dimethylamino-9,10,11,12-tetrafluorotetracyclo-[6.4.0.0.<sup>2,4</sup>0<sup>3,7</sup>]dodeca-5,8,10,12-tetraene (9) (40 mg, 2%), an unstable oil,  $\tau$  (CCl<sub>4</sub>) 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.  $C_{14}H_{15}F_{4}N$  requires C, 61.55; H, 5.55; N, 5.15%; M, 273),  $\tau$  (CCl<sub>4</sub>) 5.24 (1H, t, |J| 8 Hz), 7.47 (6H, s), and 6.8—9.0 (8H, m);  $v_{max}$  3000, 2940, 2862, 2800, 1633, 1512, 1470, 1177, 1128, 1050, 943, and 821 cm<sup>-1</sup>;  $\lambda_{max}$ . (cyclohexane) 212 ( $\epsilon$  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%;  $M^{\ddagger}$ , 287. C<sub>15</sub>H<sub>17</sub>F<sub>4</sub>N requires C, 62.7; H, 6.0; N, 4.9%; M, 287),  $\tau$  (CCl<sub>4</sub>) 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%);  $\tau$ (CCl<sub>4</sub>) 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 <sup>25</sup> J. A. Marshall and W. S. Johnson, J. Org. Chem., 1963, 28, 423. 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%;  $M^{\ddagger}$  246. C<sub>12</sub>H<sub>10</sub>F<sub>4</sub>O requires C, 58.55; H, 4.1%; M, 246),  $\tau$  (CDCl<sub>3</sub>) 7.1—7.5 (4H, m) and 8.0—8.5 (6H, m);  $\nu_{max}$ . 2940, 2875, 1710, 1515, 1480, 1125, 1050, 935, and 875 cm<sup>-1</sup>;  $\lambda_{max}$ . (cyclohexane) 264 nm ( $\varepsilon$  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-dideuterioderivative (85%),  $\tau$  (CDCl<sub>3</sub>) 7·1—7·5 (2H, m) and 8·0—8·5 (6H, m); *M*<sup>+</sup> 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<sub>13</sub>H<sub>12</sub>F<sub>4</sub>O requires C, 60.0; H, 4.65%; M, 260);  $\tau$  (CCl<sub>4</sub>) 7.0-7.5 (4H, m), 7.8-8.9 (5H, m), and 9.0 (3H, d, |J| 6 Hz);  $\nu_{max}$  1713 cm<sup>-1</sup>.

 $v_{max}$ . 1713 cm<sup>-1</sup>. *Reduction of Compound* (6).<sup>25</sup>—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-*hexahydro*-

benzocyclo-octene (12) (197 mg, 98%), m.p.  $38 \cdot 5^{\circ}$  (after sublimation) (Found: C,  $62 \cdot 4$ ; H,  $6 \cdot 25$ ; N,  $5 \cdot 15$ . C<sub>14</sub>H<sub>17</sub>F<sub>4</sub>N requires C,  $62 \cdot 55$ ; H,  $6 \cdot 2$ ; N,  $5 \cdot 1\%$ ),  $\tau$  (CDCl<sub>3</sub>)  $5 \cdot 9 - 6 \cdot 4$ (2H, m),  $7 \cdot 0 - 7 \cdot 4$  (1H, m),  $7 \cdot 83$  (6H, s), and  $7 \cdot 8 - 8 \cdot 8$ (8H, m).

Reaction of Tetrafluorobenzyne with NN-Dimethylcyclohex-1-envlamine.-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  $-70^{\circ}$  and the mixture was stirred for 0.5 h. The amine (prepared in 59%) yield <sup>26</sup>) (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 (2N;  $4 \times 25$  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%;  $M^{\ddagger}$ , 273.  $C_{14}H_{15}$ F<sub>4</sub>N requires C, 61·55; H, 5·55; N, 5·15%; M, 273),  $\tau$  (CCl<sub>4</sub>) 6·25-6·5 (1H, m), 7·69 (6H, s), 7·7-8·2 (4H, m), and 8.2—8.9 (4H, m),  $\nu_{max}$  2938, 2880, 2849, 2800, 1635, 1500, 1280, 1031, and 897 cm<sup>-1</sup>.

Removal of the ether and cyclohexanone from the nonbasic 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%;  $M^{\ddagger}$ , 246.  $C_{12}H_{10}F_4O$  requires C, 58.5; H, 4.1%; M, 246),  $\tau$  (CCl<sub>4</sub>) 3.0—3.5 (1H, m), 6.0—6.5 (1H, <sup>26</sup> W. A. White and H. Weingarten, J. Org. Chem., 1967, **32**, 213. m), and 7:4--8:5 (8H, m),  $\nu_{max.}$  1710 cm^-1,  $\lambda_{max.}$  (EtOH) 261 nm (z 960).

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