

## Cation Radicals:<sup>1</sup> Oxidative Coupling of Carbazoles, 10,11-Dihydro-5*H*-dibenz[*b,f*]azepines and Related Derivatives by 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone and Tris-(*p*-bromophenyl)ammoniumyl Salts

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Reactions of carbazoles and 10,11-dihydro-5*H*-dibenz[*b,f*]azepines with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone in the presence of acids, and with tris-(*p*-bromophenyl)ammoniumyl salts gave good yields of cation radical salts from ring coupled dimers. Corresponding reactions with iminostilbenes gave mixtures of dimers which could not be separated.

UNLIKE the oxidative coupling of acetylenes<sup>2</sup> and of phenols,<sup>3</sup> oxidative coupling of condensed hetero-aromatic molecules has not been extensively studied. Ring coupled dimers are known for carbazole,<sup>4</sup> dibenzo[*b,d*]furan,<sup>5</sup> dibenzo[*b,d*]thiophen,<sup>6</sup> phenothiazine,<sup>7</sup> acridan,<sup>8</sup> dibenzo[*b,f*]thiepin,<sup>9</sup> and 10,11-dihydrodibenz[*b,f*]thiepin.<sup>10</sup> Also dimers coupled through the heteroatom are known for carbazole,<sup>11</sup> dibenzo[*b,d*]phosphole,<sup>12</sup> and dibenzo[*b,d*]silole.<sup>13</sup>

Oxidative coupling of organic substrates<sup>14</sup> has been accomplished electrochemically,<sup>15</sup> by Ullmann, Wurtz, and Grignard reactions, and by a variety of oxidising agents including copper(II) acetate, iron(III) chloride, lead tetra-acetate, silver oxide, chromium trioxide, potassium permanganate, and sodium dichromate. Previously,<sup>16</sup> we have reported the preparation of 3,3'-bicarbazolyls by one-electron oxidation of carbazole and its derivatives, using lead tetra-acetate in glacial acetic acid containing perchloric or fluoroboric acid, and now present a more extensive investigation of the oxidation of carbazoles, 5*H*-dibenz[*b,f*]azepine (9) (iminostilbene), 10,11-dihydro-5*H*-dibenz[*b,f*]azepine (7) (iminobenzyl), and related derivatives with a variety of one-electron oxidants.

Carbazoles and related donor molecules readily form stable charge transfer complexes with quinones<sup>17,18</sup> such as 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (17), chloranil, bromanil, *etc.* However, we have observed that such complexes on treatment with protic acids (in acetic acid) or boron trifluoride-ether (in dichloromethane) rapidly give good yields of stable cation radicals from oxidatively coupled carbazoles. The interaction of DDQ and *N*-ethylcarbazole in glacial acetic containing perchloric acid affords, in quantitative yield, the dark green cation radical salt, 9,9'-diethyl-

3,3'-bicarbazoliumyl perchlorate (4). A study of the stoichiometry of this reaction revealed that the optimum yield of cation radical salt was obtained when carbazole, DDQ, and perchloric acid reacted in the molar ratios 1 : 0.75 : 5. The i.r. spectrum of the salt (4) showed absorptions at 1070, 1100, and 835 cm<sup>-1</sup> appropriate to a perchlorate salt and a 3-substituted carbazole ring, respectively. A solution of (4) prepared *in vacuo* exhibited a strong e.s.r. signal (gyromagnetic ratio, *g* 2.0048) which could not be resolved into any fine structure. The cation radical nature of the salt (4) was also demonstrated by its ability to initiate polymerisation of *N*-vinylcarbazole. Further proof of the structure was obtained by the reduction of the salt (4) using sodium dithionite, and comparison of the neutral product, 9,9'-diethyl-3,3'-bicarbazolyl (2), with an independently prepared sample.

Similar cation radical salts (5) and (6) have been prepared from *N*-isopropyl- and *N*-phenyl-carbazole, by oxidation with DDQ. The one-electron oxidant tris-(*p*-bromophenyl)ammoniumyl perchlorate (19) also oxidised carbazole and *N*-ethylcarbazole to their respective cation radical perchlorate salts (3) and (4).

There are several possible mechanisms for the formation of the 3,3'-bicarbazolyl cation radical salts from the respective neutral carbazoles,<sup>19</sup> and these are summarised in the Scheme. Quinones, and DDQ in particular, are capable of effecting the removal of either an electron, a hydrogen atom, or a hydride ion.<sup>20</sup> In the case of the carbazoles, addition of DDQ merely gives rise to charge transfer spectra and addition of acid (protonic or Lewis) is required to obtain reaction. The presence of acid in quinone dehydrogenations has been observed to acceler-

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<sup>10</sup> J. O. Jilek, V. Seidlova, E. Svatek, M. Protiva, J. Pomykacek, and Z. Sedivy, *Monatsh.*, 1965, **96**, 182.

<sup>11</sup> W. H. Perkin and S. H. Tucker, *J. Chem. Soc.*, 1921, **119**, 216; S. H. Tucker and J. McKintosh, *ibid.*, 1927, 1214.

<sup>12</sup> M. Davis and F. G. Mann, *J. Chem. Soc.*, 1964, 3770; A. D. Britt and E. T. Kaiser, *J. Org. Chem.*, 1966, **31**, 112.

<sup>13</sup> H. Gilman and R. D. Gorisch, *J. Amer. Chem. Soc.*, 1958, **80**, 3243.

<sup>14</sup> J. R. Lewis, *Chem. Ind.*, 1962, 159; 1964, 1672.

<sup>15</sup> H. Lund, *Adv. Heterocyclic Chem.*, 1970, **12**, 213.

<sup>16</sup> D. H. Iles and A. Ledwith, *Chem. Comm.*, 1968, 498.

<sup>17</sup> D. H. Iles, M. C. Lambert, and A. Ledwith, unpublished results.

<sup>18</sup> D. H. Iles, Ph.D. Thesis, Liverpool, 1969.

<sup>19</sup> S. C. Creason, J. Wheeler, and R. F. Nelson, *J. Org. Chem.*, 1972, **37**, 4440.

<sup>20</sup> D. Walker and J. D. Hiebert, *Chem. Rev.*, 1967, 153.

<sup>1</sup> Previous paper in this series, L. J. Kricka and A. Ledwith, *J.C.S. Perkin I*, 1973, 294.

<sup>2</sup> T. F. Rutledge, 'Acetylenic Compounds,' Rheinhold, London, 1968.

<sup>3</sup> A. I. Scott, *Quart. Rev.*, 1965, **19**, 1.

<sup>4</sup> M. Kuroki, *J. Synthetic Org. Chem., Japan*, 1965, **23**, 447; S. H. Tucker and T. F. Macrae, *J. Chem. Soc.*, 1933, 1520; S. H. Tucker and M. C. Nelmar, *ibid.*, p. 1523.

<sup>5</sup> H. O. Wirth, G. Waese, and W. Kern, *Macromol. Chem.*, 1965, **86**, 139; H. B. Willis, *Iowa State Coll. J. Sci.*, 1943, **18**, 98.

<sup>6</sup> H. Gilman and G. R. Wilder, *J. Org. Chem.*, 1957, **22**, 523.

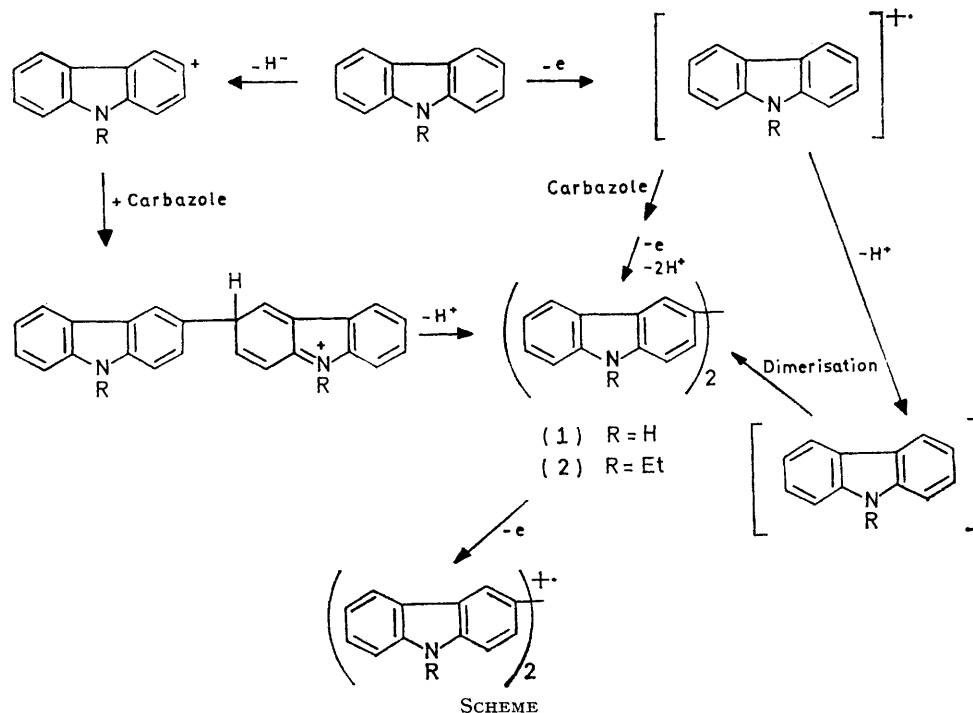
<sup>7</sup> C. Bodea and I. Silberg, *Adv. Heterocyclic Chem.*, 1968, **9**, 321, and references therein.

<sup>8</sup> V. Zanker, E. Erhardt, and J. Thies, *Ind. chim. belges*, 1967, 32 Spec. No. Pt. III, 24; F. McCapra, in 'Acridines,' ed. R. M. Acheson, 2nd edn., Wiley, London, 1973, ch. VI.

ate the dehydrogenation reaction,<sup>21</sup> and this is thought to be owing to the formation of a conjugate acid by the quinone, *e.g.* (17)  $\rightarrow$  (18). The conjugate acid (18), being more electrophilic than the quinone, would be the active oxidising species. Hydride ion abstraction by (18) would give a positively charged carbazole species and 2,3-dichloro-5,6-dicyanoquinol, whilst one-electron transfer would produce a carbazole cation radical and a semi-quinone radical. Another possibility is that under the acidic conditions the carbazole is protonated, albeit

neutral 3,3'-bicarbazolyl (see Scheme) and this is oxidised further to the 3,3'-bicarbazolyl cation radical. Yields are quantitative when 2 mole of the carbazole are treated with 3 mole of oxidant, in agreement with the proposed reaction stoichiometry.

Electrochemical studies have shown that the radical cations derived from carbazole, *N*-alkyl-, and *N*-aryl-carbazoles are unstable.<sup>24</sup> The carbazole radical cation produced at a potential of 1.2 V (s.c.e.) rapidly dimerises with loss of two protons to form 3,3'-bicarbazolyl which



very weakly, and the quaternary salt produced could, by loss of a hydrogen atom, give the carbazolyl cation radical.

Related studies of the oxidation of phenothiazine by a series of quinones in acidic acetonitrile solution,<sup>22</sup> have revealed that the primary process is a one-electron transfer to form a phenothiazine cation radical. However, for the reaction of carbazoles with DDQ, it is not possible to rule out hydride ion abstraction as the primary oxidation step.

Confirmation of the role of electron transfer in oxidative coupling reactions is provided by oxidations using the ammoniumyl salts (19) and (20) which proceed *via* an unambiguous one-electron transfer pathway.<sup>23</sup> The initial step in the oxidation of carbazole by the ammoniumyl salt (19) is the formation of a carbazole cation radical which ultimately dimerises\* to form the

may undergo further oxidation at this potential to produce a quinonoidal dication.

Iminobibenzyl (7) and 5-methyliminobibenzyl (8) are oxidised by DDQ and by the ammoniumyl salt (20) to the cation radical perchlorates (11) and (12) and hexachloroantimonates (13) and (14), respectively. Each salt was reduced by sodium dithionite to its respective neutral 10,10',11,11'-tetrahydrobi-(5*H*-dibenz[*b,f*]azepine) (15) and (16). The i.r. spectra of the coupled products (15) and (16) showed absorptions in the region 805–815 cm<sup>-1</sup> appropriate to 2-substitution [*cf.* (2,8-dibromo)-iminobibenzyl,  $\nu_{\text{max}}$  810 cm<sup>-1</sup> (2-substitution) and 3-acetyl-5-propionyl(imino)bibenzyl,  $\nu_{\text{max}}$  830 cm<sup>-1</sup> (3-substitution)<sup>25</sup>] and were identical with those of authentic samples prepared by oxidation of iminobibenzyl and 5-methyliminobibenzyl by sodium dichromate in acetic acid. Coupling of cation radicals

\* It is not possible from the present data to distinguish between coupling mechanisms involving (a) dimerisation of two cation radicals followed by loss of two protons or (b) reaction of a cation radical with its neutral precursor followed by loss of an electron and two protons. However, the latter pathway must be considered, on account of the high reactivity of these aromatic derivatives to electrophilic substitution.

<sup>21</sup> R. P. Linstead, E. A. Braude, and L. M. Jackman, *J. Chem. Soc.*, 1954, 3544; 1960, 3166.

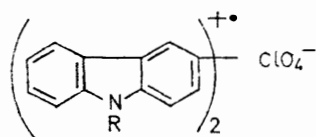
<sup>22</sup> R. Foster and P. Hanson, *Biochim. Biophys. Acta*, 1966, **112**, 482.

<sup>23</sup> A. Ledwith, *Accounts Chem. Res.*, 1972, **5**, 133.

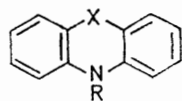
<sup>24</sup> J. F. Ambrose and R. F. Nelson, *J. Electrochem. Soc.*, 1968, **115**, 1159.

<sup>25</sup> L. J. Kricka and A. Ledwith, *J.C.S. Perkin I*, 1973, 859.

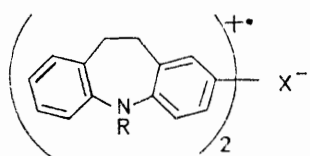
derived from iminobibenzyl at the 2-position is in accord with the related electrophilic substitution of iminobenzyl which affords 2- and 2,8-substituted derivatives.<sup>26</sup>



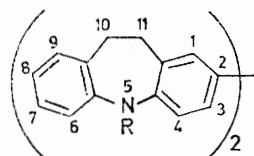
- (3) R = H  
(4) R = Et  
(5) R = Pr<sup>i</sup>  
(6) R = Ph



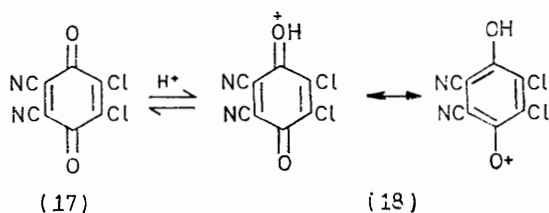
- (7) X = CH<sub>2</sub>CH<sub>2</sub>, R = H  
(8) X = CH<sub>2</sub>CH<sub>2</sub>, R = Me  
(9) X = CH=CH, R = H  
(10) X = CH=CH, R = Me



- (11) R = H, X = ClO<sub>4</sub>  
(12) R = Me, X = ClO<sub>4</sub>  
(13) R = H, X = SbCl<sub>6</sub>  
(14) R = Me, X = SbCl<sub>6</sub>

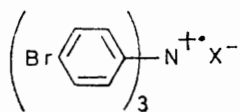


- (15) R = H  
(16) R = Me



(17)

(18)



- (19) X = ClO<sub>4</sub>  
(20) X = SbCl<sub>6</sub>

Related oxidations of iminostilbene and 5-methyliminostilbene gave complex mixtures of intensely coloured products. Mass spectrometric analysis indicated that these materials were dimeric but it was not possible to separate and identify the individual constituents. However, it seems likely that iminostilbenes may couple at both the 2- and 10(11)-positions.

#### EXPERIMENTAL

I.r. spectra were recorded for Nujol mulls. <sup>1</sup>H N.m.r. spectra were measured at 60 MHz for solutions in deuteriochloroform with tetramethylsilane as internal standard. Mass spectra were measured by the Physico-Chemical

<sup>26</sup> L. J. Kricka and A. Ledwith, *Chem. Rev.*, in the press.

<sup>27</sup> F. A. Bell, A. Ledwith, and D. C. Sherrington, *J. Chem. Soc. (C)*, 1969, 2719.

Measurements Unit at Harwell. Alumina for chromatography was 'Camag' M.F.C. Neutral (Hopkin and Williams). Acetic acid was refluxed with acetic anhydride, and methylene chloride refluxed over calcium hydride, prior to fractional distillation. Tris-(*p*-bromophenyl)-ammoniumyl hexachloroantimonate and perchlorate were prepared as described.<sup>27</sup> 2,3-Dichloro-5,6-dicyanobenzoinone (DDQ) (Koch-Light) was recrystallised from benzene-chloroform and had m.p. 202° (decomp.). 5-Methyliminostilbene, m.p. 141–143° (lit.,<sup>28</sup> 143–144.5°) was prepared by treatment of iminostilbene with thallium ethoxide-methyl iodide.<sup>29</sup> 9,9-Diethyl-3,3'-bicarbazolyl (2) was obtained by oxidation of *N*-ethylcarbazole with sodium dichromate in a mixture of acetic and conc. sulphuric acid. The crude product was purified by chromatography on a column of neutral alumina made up in benzene. Elution with benzene afforded (2), m.p. 193–194° (lit.,<sup>30</sup> 188–190°) as yellow plates (Found: C, 86.5; H, 6.2; N, 7.3. Calc. for C<sub>28</sub>H<sub>24</sub>N<sub>2</sub>: C, 86.6; H, 6.2; N, 7.2%).

5-Methyliminobibenzyl (76%), m.p. 106–107° (lit.,<sup>28</sup> 107–108°) was prepared by the reaction of iminobibenzyl and powdered potassium hydroxide with methyl iodide at room temperature.<sup>31</sup>

10,10',11,11'-Tetrahydro-2,2'-bi-(5H-dibenz[b,f]azepine) (15).—Sodium dichromate (3.2 g) was added during 1 min to a stirred ice-cooled solution of iminobibenzyl (5.0 g) in glacial acetic acid (500 ml) containing sulphuric acid (30 ml). After 10 min, aqueous sodium hydrogen sulphite (500 ml; 40% w/w) was added and the mixture refluxed for 3 h. The mixture was then filtered and the solid extracted repeatedly with acetone. Evaporation of the combined acetone extracts afforded the crude product (3.3 g, 66%). A portion of this product (1.0 g) was dissolved in the minimum amount of chloroform and chromatographed on a short column of neutral alumina made up in benzene. Ether-benzene (1 : 1 v/v) eluted the dimer (15) (0.2 g), m.p. 300–302° (decomp.) (Found: C, 86.5; H, 6.2; N, 7.3. C<sub>28</sub>H<sub>16</sub>N<sub>2</sub> requires C, 86.6; H, 6.2; N, 7.2%),  $\nu_{\max}$  3350 (N–H), 1610, 1590 (benzene ring), 1500br, 1335, 935, 875, 505, and 640 cm<sup>-1</sup>,  $\tau$  [(CD<sub>3</sub>)<sub>2</sub>SO] 1.7br (2H, NH), 2.6–3.1 (14H, m, ArH), 7.00 (8H, s, ArCH<sub>2</sub>), *m/e* 388 (*M*<sup>+</sup>, 100%), 389 (*M* + 1, 30), 195 (20), and 193 (13).

Similarly, oxidation of 5-methyliminobibenzyl with sodium dichromate afforded the crude coupled product (3.5 g, 70%). A portion of this material (1.0 g) was dissolved in the minimum quantity of chloroform and chromatographed on a short column of alumina made up in benzene. Elution with light petroleum (b.p. 30–40°) and light petroleum (b.p. 30–40°)-benzene (3 : 7 v/v) afforded 10,10',11,11'-tetrahydro-5,5'-dimethyl-2,2'-bi-(5H-dibenz[b,f]-azepine) (16) (0.8 g), as needles, m.p. 169–170° [from light petroleum (b.p. 60–80°)-benzene (1 : 1 v/v)] (Found: C, 86.1; H, 7.1; N, 6.7. C<sub>30</sub>H<sub>28</sub>N<sub>2</sub> requires C, 86.5; H, 6.8; N, 6.7%),  $\nu_{\max}$  1595 (benzene ring), 1490br, 1330, 1260, 1225, 1110, 815, and 750 cm<sup>-1</sup>,  $\tau$  2.5–3.2 (14H, m, ArH), 6.64 (6H, s, NCH<sub>3</sub>), and 6.82 (8H, s, ArCH<sub>2</sub>), *m/e* 416 (*M*<sup>+</sup>, 100%), 417 (*M* + 1, 35), 401 (*M* – Me, 12), 385 (*M* – 2Me, 8), 208 (9), and 196 (11).

Reaction of *N*-Ethylcarbazole with DDQ.—A solution of DDQ (0.85 g) in glacial acetic acid (20 ml) was added to a

<sup>28</sup> R. Huisgen, E. Laschtuvka, and F. Bayerlein, *Chem. Ber.*, 1960, 93, 392.

<sup>29</sup> L. J. Kricka and A. Ledwith, *J.C.S. Perkin I*, 1972, 2292.

<sup>30</sup> P. Maitland and S. H. Tucker, *J. Chem. Soc.*, 1927, 1388.

<sup>31</sup> H. Heaney and S. V. Ley, *J.C.S. Perkin I*, 1973, 499.

stirred mixture of *N*-ethylcarbazole (0.98 g), aqueous perchloric acid (70% w/w; 3 ml), and glacial acetic acid (25 ml). After stirring 0.5 h at room temperature the precipitate obtained was filtered and washed repeatedly with warm diethyl ether and dried to afford 9,9'-diethyl-3,3'-bicarbazolyliumyl perchlorate (4) (1.45 g, 95%) as a dark green powder\* (Found: C, 65.3; H, 5.3; N, 5.4. Calc. for  $C_{28}H_{34}ClN_2O_4$ : C, 64.6; H, 5.7; N, 6.5%).  $\nu_{\max}$  1615, 1595 (benzene ring), 1560, 1440, 1220, 1150, 1100, 1070 (perchlorate), 835 (3-substitution), 725, 715, and 705  $cm^{-1}$ ,  $m/e$  388 ( $M^+$ , <1%), 102/100 ( $HClO_4$ , 25/75), 87 (16), 85/83 ( $ClO_3$ , 32/100), and 69/67 ( $ClO_2$ , 20/60).

Similarly prepared were 9,9'-di-isopropyl-3,3'-bicarbazolyliumyl perchlorate (5) (90%),  $\nu_{\max}$  1605, 1590 (benzene ring), 1560, 1340br (perchlorate), 900br, 835 (3-substitution), 800, 750, and 710  $cm^{-1}$ ,  $\lambda_{\max}$  ( $CH_2Cl_2$ ) 390 and 880 nm; and 9,9'-diphenyl-3,3'-bicarbazolyliumyl perchlorate (88%),  $\nu_{\max}$  1605, 1595 (benzene ring), 1560, 1240, 1140, 1020, 1100br (perchlorate), 940, 835 (3-substitution), 800, 760, 755, and 710  $cm^{-1}$ ,  $\lambda_{\max}$  410 and 850 nm. Both materials were intractable green powders.

**Reduction of 9,9'-Diethyl-3,3'-bicarbazolyliumyl Perchlorate (4) by Sodium Dithionite.**—A stirred suspension of the salt (4) (0.4 g) in acetone (100 ml) was treated with saturated aqueous sodium dithionite, whereupon the mixture changed from green to yellow and finally gave a brown solution. This was extracted with benzene and the extract washed and dried ( $MgSO_4$ ). Evaporation of the extract gave a brown solid, which was dissolved in the minimum quantity of chloroform and chromatographed on a short column of neutral alumina made up in light petroleum. Elution with benzene afforded 9,9'-diethyl-3,3'-bicarbazolyl (0.1 g), m.p. 193—194° (lit.,<sup>30</sup> 188—190°) (Found: C, 86.5; H, 6.1; N, 7.3. Calc. for  $C_{28}H_{24}N_2$ : C, 86.6; H, 6.2; N, 7.2%).  $\nu_{\max}$  1600 (benzene ring), 1340, 1230, 1150, 1110, 885, 805 (3-substitution), 745, and 730  $cm^{-1}$ ,  $m/e$  388 ( $M^+$ , <1%), 196 (10), 195 (70), 180 (100), 178 (70), 167 (18), and 152 (16). A molecular weight determination in a vapour pressure osmometer gave a value of 382 (required 388).

**Oxidation of 9,9'-Diethyl-3,3'-bicarbazolyl.**—9,9'-Diethyl-3,3'-bicarbazolyl (0.1 g) was dissolved in hot glacial acetic acid. Aqueous perchloric acid (0.5 ml; 70% w/w) and a solution of DDQ (0.04 g) in glacial acetic acid (*ca.* 5 ml) were added to the cooled solution, whereupon a green colouration developed. Addition of ether precipitated a green solid which was filtered off, washed with ether, and dried. This material was 9,9'-diethyl-3,3'-bicarbazolyliumyl perchlorate (0.11 g, 88%) and had an i.r. spectrum identical with that of an authentic sample.

**Reaction of *N*-Ethylcarbazole with Tris-(*p*-bromophenyl)-ammoniumyl Perchlorate.**—A solution of the ammoniumyl salt (19) (1.75 g, 3 mmol) in dichloromethane (220 ml) was added to a stirred solution of *N*-ethylcarbazole (0.39 g, 2 mmol) in dichloromethane (20 ml). A green precipitate formed and this was filtered off, washed with ether, and dried to afford 9,9'-diethyl-3,3'-bicarbazolyliumyl perchlorate (4) (0.4 g, 83%). The i.r. and u.v. spectra of this material were identical with those of an authentic sample. Reduction of this material with aqueous sodium dithionite afforded 9,9'-diethyl-3,3'-bicarbazolyl, m.p. 193—194° (lit.,<sup>30</sup> 188—190°).

Similarly, the reaction of carbazole (0.24 g) with tris-(*p*-bromophenyl)ammoniumyl perchlorate (1.75 g) afforded the

\* This cation radical salt, in common with the other prepared, could not be obtained analytically pure.

dark green cation radical salt, 3,3'-bicarbazolyliumyl perchlorate (3) (0.62 g, 85%) which was reduced with aqueous sodium dithionite. The crude product was chromatographed on a short column of neutral alumina made up in light petroleum. Benzene eluted 3,3'-bicarbazolyl, m.p. >300° (lit.,<sup>4</sup> >300°) as a yellow-green powder (from anisole) (Found: C, 85.3; H, 5.3; N, 7.9. Calc. for  $C_{24}H_{16}N_2$ : C, 86.7; H, 4.8; N, 8.4). The i.r. spectrum of this material was identical with that of an authentic sample.

**Reaction of Iminobibenzyl with Tris-(*p*-bromophenyl)-ammoniumyl Hexachloroantimonate.**—A solution of the ammoniumyl salt (20) (5.0 g) in dichloromethane (30 ml) was added to a stirred solution of iminobibenzyl (0.85 g) in dichloromethane (70 ml). After 0.5 h the green solution was filtered and the solid product washed repeatedly with ether to afford 10,10',11,11'-tetrahydro-2,2'-bi-(5*H*-dibenz-[*b,f*]azepinyl)iumyl hexachloroantimonate (13) (1.5 g, 95%), as a dark green powder\* (Found: C, 41.2; H, 3.6. Calc. for  $C_{28}H_{24}Cl_6N_2Sb$ : C, 46.5; H, 3.3%),  $\nu_{\max}$  3300br (NH), 1610, 1590 (benzene ring), 1200, 890, and 770  $cm^{-1}$ .

Similarly, reaction of 5-methyliminobibenzyl with the ammoniumyl salt (20) afforded 10,10',11,11'-tetrahydro-5,5'-dimethyl-2,2'-bi-(5*H*-dibenz-[*b,f*]azepinyl)iumyl hexachloroantimonate (14) (1.4 g, 92%) as a dark blue-green powder,  $\nu_{\max}$  1600br (benzene ring), 1150br, 1090br, and 800br  $cm^{-1}$ .

**Reduction of the Cation Radical Salt (13) by Sodium Dithionite.**—An aqueous solution of sodium dithionite was added to a suspension of the hexachloroantimonate (13) (1.5 g) in acetone (50 ml) and the mixture was stirred at room temperature for 3 h. The brown mixture was filtered free of the antimony sludge, and the sludge washed with dichloromethane. The aqueous mixture was extracted with dichloromethane and the extracts and washings combined and dried ( $MgSO_4$ ). Evaporation afforded an oily solid which was dissolved in benzene and chromatographed on a short column of neutral alumina made up in benzene. Ether-benzene (2:8 v/v) eluted the bidibenzazepine (15) (0.45 g, 86%), m.p. 295—297° (decomp.). The i.r., n.m.r., and mass spectra of this material were identical with those of an authentic sample.

Similarly, reduction of the hexachloroantimonate (14) afforded, after work-up, a brown oil which was chromatographed on a short column of alumina made up in benzene. Elution with benzene afforded the bidibenzazepine (16) (0.30 g, 39%), m.p. 185—190°. The i.r. and n.m.r. spectra of this material were identical with those of an authentic sample, but the mass spectrum indicated that the product was contaminated with tris-(*p*-bromophenyl)amine.

**Reaction of Iminobibenzyl with DDQ.**—A solution of DDQ (0.85 g) in glacial acetic acid (20 ml) was added to a stirred solution of iminobibenzyl (1.0 g) in glacial acetic acid (25 ml) containing aqueous perchloric acid (3 ml; 70% w/w). After 1 h the mixture was filtered and the product washed repeatedly with ether and dried to afford 10,10',11,11'-tetrahydro-2,2'-bi-(5*H*-dibenz-[*b,f*]azepinyl)iumyl perchlorate (11) (1.4 g, 92%),  $\nu_{\max}$  3300br (NH), 1605, 1585 (benzene ring), 1300br, 1160, 1100br, 1050br (perchlorate), 930, 890, and 760  $cm^{-1}$ . Reduction of the salt with sodium dithionite and chromatography of the product afforded the bidibenzazepine (15) (0.3 g, 45%), m.p. 300—302° (decomp.).

Similarly, DDQ and 5-methyliminobibenzyl afforded 10,10',11,11'-tetrahydro-5,5'-dimethyl-2,2'-bi-(5*H*-dibenz-[*b,f*]azepinyl)iumyl perchlorate (12) (1.45 g, 97%) as a dark

brown powder,  $\nu_{\max}$  1400, 1200br, 1090br (perchlorate), 890, 800, and 770  $\text{cm}^{-1}$ . Reduction with sodium dithionite afforded the bidibenzazepine (16) (0.35 g, 30%), m.p. 169—170° [from benzene-petrol (1 : 1 v/v)].

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