

# Studies on Indoles, Carbazoles, and Related Compounds. I. Carbazole Leuco Derivatives Related to 4,4'-Diaminodiphenylmethanes. Bis(3-carbazolyl)methanes and Bis(9-carbazolyl)methanes

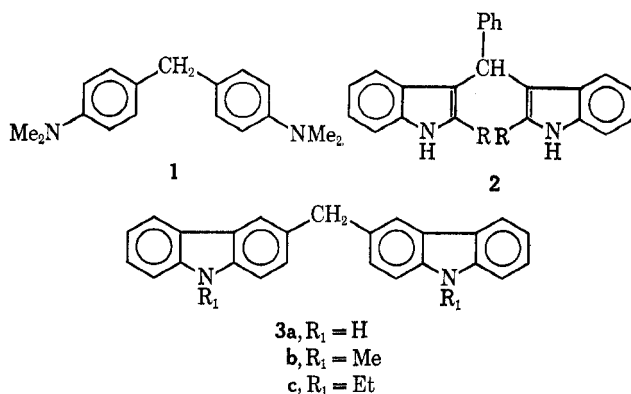
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Received November 26, 1969

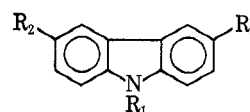
Bis(3-carbazolyl)methane and some bis(9-alkyl-3-carbazolyl)methanes have been synthesized, the former *via* the Borsche synthesis from 4,4'-dihydrazinodiphenylmethane and the latter by condensation of 6-blocked 9-alkylcarbazoles with formaldehyde, followed by removal of the blocking 6 substituent. These compounds are compared and contrasted with the products obtained from the acetic acid catalyzed condensation of carbazole, or of unblocked 9-alkylcarbazoles, with formaldehyde. Infrared and proton magnetic resonance studies establish that the carbazole-formaldehyde condensation product is bis(9-carbazolyl)methane, in contrast to some literature reports.

In a comparative study of leuco compounds related to 4,4'-diaminodiphenylmethane derivatives, *e.g.*, tetramethyl base **1**, and to phenylbis(3-indolyl)methanes (leuco rosindoles) **2**, we recently required bis(3-carbazolyl)methane (**3a**) and some bis(9-alkyl-3-carbazolyl)methanes, *e.g.*, **3b** and **3c**. According to three standard reference works,<sup>1-3</sup> these latter compounds



are accessible *via* the direct acid-catalyzed condensation of carbazole, or 9-alkylcarbazoles, respectively, with formaldehyde (or formaldehyde progenitors), analogous to, for example, the well-known preparation of tetramethyl base **1** from formaldehyde and N,N-dimethylaniline in acid solution. On consulting the original literature, however, it became apparent that some confusion and conflicting conclusions exist as to the final products obtained from carbazole, or 9-alkylcarbazoles, and formaldehyde in various acidic media.<sup>4-20</sup> The

products obtained from such reactions vary with the reaction conditions. Thus, the reaction product from carbazole and formaldehyde in concentrated sulfuric acid forms a blue solution or precipitates as a blue dye,<sup>5,7,8,11,15,16</sup> while under less stringent conditions, *e.g.*, carbazole and formaldehyde (or formaldehyde progenitors) in acetic acid, the major product is a bis-carbazolylmethane, mp "above 280°,"<sup>4,6</sup> 287°,<sup>10</sup> 301-303°.<sup>13</sup> This compound is also obtained by warming 9-hydroxymethylcarbazole (**4a**) in acetic acid.<sup>9</sup> Where-



- 4a**,  $R_1 = CH_2OH$ ;  $R_2 = R_3 = H$   
**b**,  $R_1 = CH_2OCOCH_3$ ;  $R_2 = R_3 = H$   
**c**,  $R_1 = H$ ;  $R_2 = R_3 = Cl$   
**d**,  $R_1 = H$ ;  $R_2 = R_3 = Br$   
**e**,  $R_1 = H$ ;  $R_2 = R_3 = I$   
**f**,  $R_1 = Et$ ;  $R_2 = H$ ;  $R_3 = CHO$   
**g**,  $R_1 = Et$ ;  $R_2 = Br$ ;  $R_3 = CHO$

as the structure of the blue dye still remains obscure, the bis-carbazolylmethane has been reported by some workers<sup>4,13,19</sup> as bis(9-carbazolyl)methane (**5a**) but by others<sup>6,10,14a</sup> as bis(3-carbazolyl)methane (**3a**). The latter assignment has been generally accepted previously,<sup>1-3</sup> mainly owing to (i) a suggestion<sup>10</sup> that a free 3 position is necessary before condensation can occur and (ii) the preparation of authentic bis(9-carbazolyl)methane, mp 314-315°, from 9-acetoxymethylcarbazole (**4b**) and carbazolylmagnesium iodide.<sup>14a</sup> However,

text as to the point of formaldehyde condensation on the carbazole molecule. A condensed structural formula (p 37 of their paper) indicates, however, that these workers also preferred the 9,9'-condensed structure **5a**.

(14) (a) K. Mizuch, *Zh. Obshch. Khim.*, **16**, 1471 (1946); (b) K. Mizuch and Ts. M. Gel'fer, *J. Appl. Chem. USSR*, **19**, 939 (1946); (c) *Dokl. Akad. Nauk SSSR*, **79**, 807 (1951); (d) K. G. Mizuch, N. M. Kasatkin, and Ts. M. Gel'fer, *Zh. Obshch. Khim.*, **27**, 189 (1957).

(15) K. Fürst, *Mikrochem. Ver. Mikrochim. Acta*, **33**, 348 (1948).

(16) M. Cermak, *Chem. Listy*, **45**, 35 (1951).

(17) F. Muzik and Z. J. Allan, *Collect. Czech. Chem. Commun.*, **22**, 641 (1957).

(18) (a) V. F. Traven and B. I. Stepanov, *Tr. Mosk. Khim. Tekhnol. Inst.*, **48**, 118 (1965); *Chem. Abstr.*, **65**, 12159 (1966); (b) V. F. Traven, V. A. Smrček, and B. I. Stepanov, *Khim. Geterotsikl. Soedin.*, 568 (1967); *Chem. Abstr.*, **68**, 39407 (1968); (c) V. F. Traven, V. A. Plakhov, and B. I. Stepanov, *Khim. Geterotsikl. Soedin.*, 756 (1967); *Chem. Abstr.*, **68**, 104884 (1968).

(19) S. Nakade and M. Imoto, *Kogyo Kagaku Zasshi*, **69**, 100 (1966); *Chem. Abstr.*, **65**, 3822 (1966).

(20) S. Nakade, U. Funayama, and A. Gomi, *Kogyo Kagaku Zasshi*, **69**, 2214 (1966); *Chem. Abstr.*, **66**, 116188 (1967).

(1) "Beilstein's Handbuch der Organischen Chemie," 4th ed, Springer-Verlag, Berlin: (a) Vol. 20, Hauptwerk, p 436; (b) Vol. 23, Hauptwerk, p 239; 1st Suppl., p 96.

(2) W. C. Sumpter and F. M. Miller, "The Chemistry of Heterocyclic Compounds," Vol. 8, A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1954, pp 107-108.

(3) E. H. Rodd, "Chemistry of Carbon Compounds," Vol. 4, Elsevier Publishing Co., Amsterdam, 1957, p 124.

(4) G. Pulvermacher and W. Loeb, *Chem. Ber.*, **25**, 2766 (1892).

(5) E. Votocek, *Rozpravy Cesk. Akad.*, **22**, 5 (1896); *Chem. Zentralbl.*, **67** (II), 490 (1896).

(6) E. Votocek and V. Vesely, *Chem. Ber.*, **40**, 414 (1907).

(7) H. Ditz, *Chem.-Ztg.*, **31**, 486 (1907); *Chem. Zentralbl.*, **78** (II), 33 (1907).

(8) E. Gabutti, *Boll. Chim. Farm.*, **46**, 349 (1907); *Chem. Zentralbl.*, **78** (II), 98 (1907).

(9) M. Lange, German Patent 256,757 (1913).

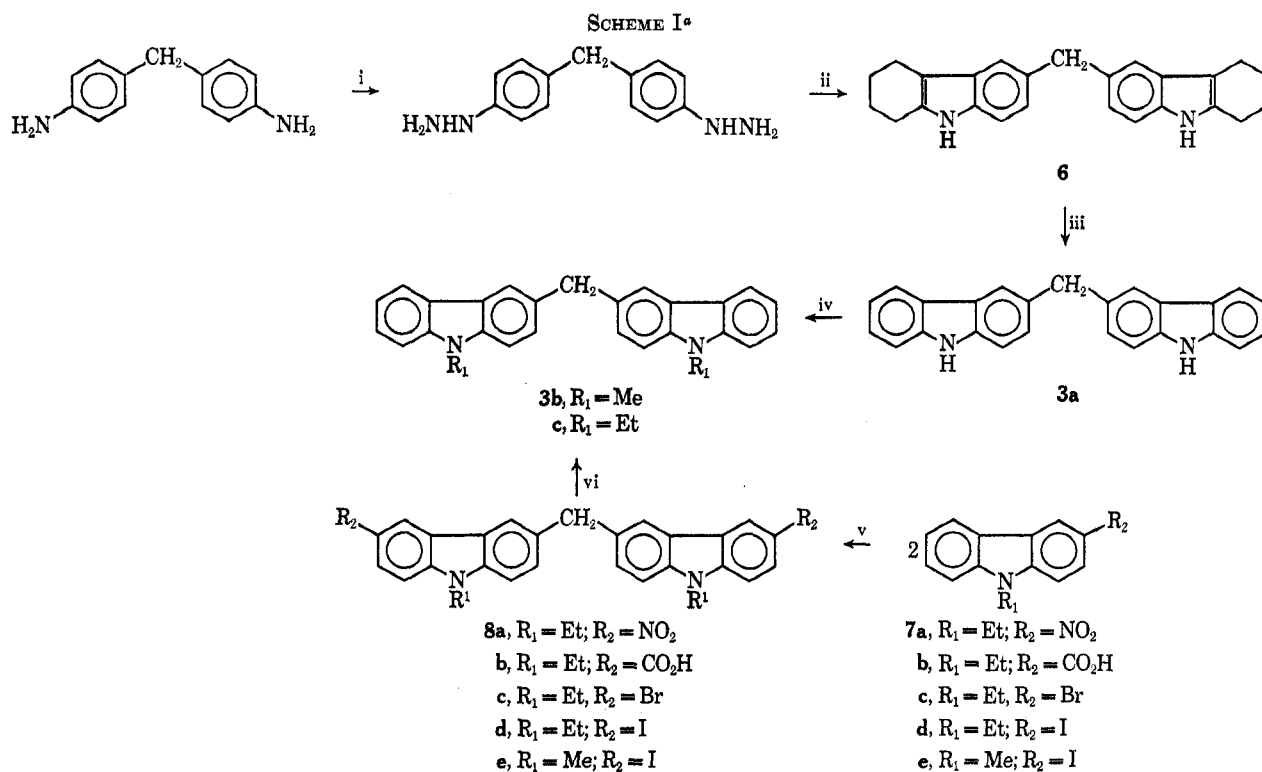
(10) S. Dutt, *J. Chem. Soc.*, **125**, 802 (1924).

(11) Z. Dische, *Biochem. Z.*, **189**, 77 (1927); *Chem. Abstr.*, **22**, 559 (1928).

(12) G. Kränzlein and R. Deresser, German Patent 699,774 (1940).

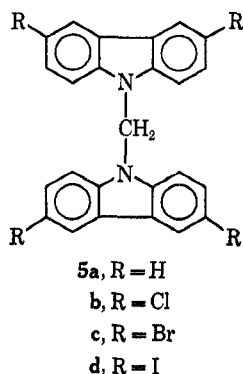
(13) J. R. Feldman and E. C. Wagner, *J. Org. Chem.*, **7**, 31 (1942).

These workers referred to the carbazole-formaldehyde condensation product simply as "methylenebiscarbazole," with no opinion expressed in their



<sup>a</sup> Reagents: i, HNO<sub>2</sub>, SnCl<sub>4</sub>-HCl; ii, cyclohexanone, AcOH; iii, Pd-C; iv, dialkyl sulfate; v, CH<sub>2</sub>O, H<sup>+</sup>; vi, Li-*t*-BuOH-THF (on 8c) or LiAlH<sub>4</sub> (on 8d, 8e).

it has been shown more recently<sup>17</sup> that 3,6-dichlorocarbazole (4c) and 3,6-dibromocarbazole (4d) readily condense with formaldehyde, yielding 5b and 5c, respec-



tively. Finally, another report<sup>21</sup> describes the isolation of a product alleged to be bis(3-carbazolyl)methane (3a), mp 234°.

We have accordingly reexamined the products obtained from (a) carbazole and formaldehyde in acetic acid,<sup>4,18</sup> (b) carbazole and methylal in acetic acid,<sup>6</sup> (c) 9-hydroxymethylcarbazole in acetic acid,<sup>9</sup> and (d) 9-carbazolylmagnesium iodide and 9-acetoxymethylcarbazole in ether.<sup>14a</sup> After purification by crystallization from N,N-dimethylformamide or from benzene, the products from all routes were identical with respect to melting point (314–317°), infrared spectra, and nmr spectra. A typical infrared spectrum of the product showed the complete absence of a -NH group and the typical benzene substitution patterns at 700–770 and 1700–1950 cm<sup>-1</sup>, characteristic of 1,2-substituted benzene rings only (equivalent to no nuclear substituents in the carbazole ring system); these findings are in ex-

cellent agreement with structure 5a and preclude the product being the 3,3 isomer 3a. The nmr spectrum exhibits signals for 16 aromatic protons and two methylene protons and is thus also in accord with structure 5a; absorptions occur at δ 6.9 (doublet of doublets, 4 H, 4 and 5 nuclear carbazole protons), 5.9–6.5 (multiplet, 12 H, remaining carbazole nuclear protons), and 5.7 (singlet, 2 H, methylene protons). The major product from each of the mild acid-catalyzed reactions, therefore, is bis(9-carbazolyl)methane (5a), as originally postulated by Pulvermacher and Loeb.<sup>4</sup>

The 9,9'-condensed structure of the carbazole-formaldehyde product was confirmed by unambiguous synthesis. Acid-catalyzed condensation of 3,6-diiodocarbazole (4e) with formaldehyde affords bis(3,6-diiodo-9-carbazolyl)methane (5d), analogous to the similar condensation products 5b and 5c obtained by Muzik and Allan<sup>17</sup> from 3,6-dichlorocarbazole and 3,6-dibromocarbazole; in these compounds, no possibility exists for 3,3 condensation. Reductive deiodination of 5d by means of lithium aluminum hydride in tetrahydrofuran affords bis(9-carbazolyl)methane 5a, identical in all respects with the product obtained from the direct carbazole-formaldehyde condensations.

We synthesized the required bis(3-carbazolyl)methane (3a) apparently for the first time, *via* the more extended Borsche tetrahydrocarbazole synthesis,<sup>22,23</sup> Scheme I. The preparation of the intermediate bis(5,6,7,8-tetrahydro-3-carbazolyl)methane (6) has been described.<sup>23</sup> Dehydrogenation of this material with palladium on charcoal<sup>24</sup> gave 3a, mp 350–352°. The

(22) W. Borsche, A. Witte, and W. Bothe, *Justus Liebigs Ann. Chem.*, **359**, 49 (1908).

(23) (a) W. Borsche and G. A. Kienitz, *Chem. Ber.*, **43**, 2335 (1910); (b) W. Borsche and R. Manteuffel, *ibid.*, **67B**, 144 (1934).

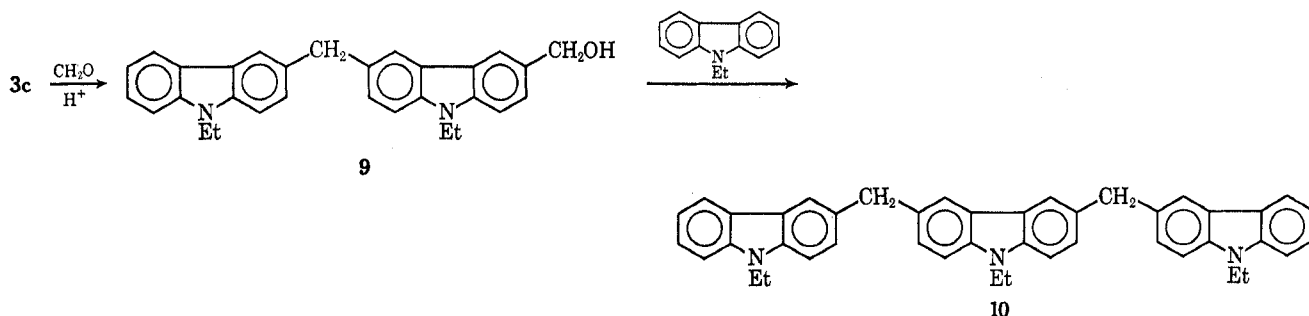
(24) (a) E. C. Horning, M. G. Horning, and G. N. Walker, *J. Amer. Chem. Soc.*, **70**, 3935 (1948); (b) P. H. Carter, S. G. P. Plant, and M. Tomlinson, *J. Chem. Soc.*, 2210 (1957).

(21) D. Jerchel and H. Fischer, *Chem. Ber.*, **88**, 1595 (1955).

infrared spectrum of the product was in excellent agreement with the required structure, showing absorption peaks at 725 and 750  $\text{cm}^{-1}$  (1,2-disubstituted benzene ring), 800 (1,2,4-trisubstituted benzene ring), and 3300 (NH). The nuclear magnetic resonance spectrum (in DMSO) exhibits absorptions at  $\delta$  7.7 (doublet, 4 H, 4 and 5 nuclear protons), 6.5–7.3 (multiplet, 10 H, remaining aromatic protons), and 3.9 (singlet, 2 H, 3,3-methylene protons), all relative to DMSO at 2.25. At the concentration employed, the NH protons appeared at  $\delta$  9.7 (very broad peak).

This material is clearly distinct from the above bis(9-carbazolyl)methane, mp 314–317°, and it appears to be also distinct from another compound, mp 234°, re-

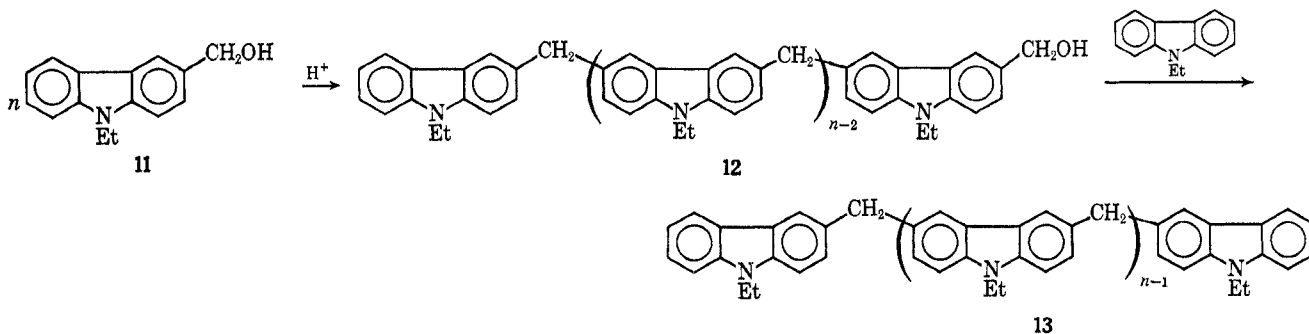
ported on the polymeric nature of these products. We also found this to be the case. The material obtained from the direct condensation of 9-ethylcarbazole with formaldehyde was an amorphous solid (mol wt 1600) which melted over a wide range. The formation of polymeric resins has also been observed in the analogous diphenylamine-formaldehyde condensation reaction.<sup>27</sup> The polymerization reaction may proceed *via* the unoccupied 6,6' nuclear positions of the initially formed bis(9-alkyl)-3-carbazolyl)methane, these positions being readily accessible for further attack and subsequent chain growth, *via* intermediates such as **9**, leading to **10**. The process may then be repeated on **10**, leading to higher oligomers.



ported by Jerchel and Fischer<sup>21</sup> as bis(3-carbazolyl)methane.

We then turned our attention to synthesizing the alkylated leuco derivatives, the bis(9-alkyl-3-carbazolyl)methanes, *e.g.*, **3b** and **3c**. Although, as shown above, the preferred site of reaction in N-unsubstituted carbazoles with formaldehyde (or protonated formaldehyde intermediates) is the N position, it appeared that, if this position were occupied, *viz.* by an alkyl group, then substitution would be directed to the *para* nuclear position, *i.e.*, the 3 position. We were thus initially hopeful that condensation of 9-methylcarbazole and 9-ethylcarbazole with formaldehyde would lead to

Alternatively, the process may partly involve self-condensation of the corresponding 3-hydroxymethyl-9-alkylcarbazole **11**, formed initially *in situ* from 9-ethylcarbazole and formaldehyde, the chain growth being finally terminated by reaction of the resultant long-chain methylol compound **12** with 9-ethylcarbazole. The facile self-condensation of **11** was readily demonstrated by treatment of this material, prepared separately from 9-ethylcarbazole-3-carboxaldehyde, with warm acetic acid. The resultant product, which softened at 157° and finally melted at 163–164°, had an average molecular weight of 1600–1800, *i.e.*,  $n = 8$  or 9 in **12**.



the required **3b** and **3c**, respectively. The only literature reports on this reaction prior to the commencement of our study appear to be a passing mention by Votocek and Vesely,<sup>6</sup> with no experimental details, and a note in an early German patent<sup>25</sup> which describes the preparation of "di-9-ethylcarbazylmethane" by condensation of 9-ethylcarbazole with formaldehyde in acetic acid in the presence of a trace of mineral acid. Kränzlein and Dereser<sup>12</sup> have commented, however, that such condensation products are nonhomogeneous resinous materials and recent patent claims<sup>26</sup> have also com-

These conjectures are supported by the observation of Kränzlein and Dereser<sup>12</sup> that 9-alkylcarbazoles containing one occupied *para* position, *viz.* 3-nitro-9-ethylcarbazole (**7a**) (Scheme I) or 9-ethylcarbazole-3-carboxylic acid (**7b**) condense smoothly with formaldehyde in acetic acid solution to give the corresponding bis(6-nitro-9-ethyl-3-carbazolyl)methane (**8a**) and bis(6-carboxy-9-ethyl-3-carbazolyl)methane (**8b**), respectively, as crystalline materials in good yields; in these cases the linear chain growth cannot occur.

The authentic bis(9-alkyl-3-carbazolyl)methanes **3b** and **3c** were obtained by blocking the carbazole 6 posi-

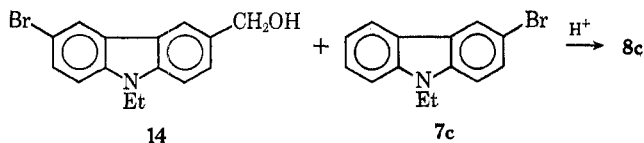
(25) German Patent 293,578 (1913).

(26) (a) French Patent 1,399,095 (1965); (b) U. S. Patent 3,240,597 (1966).

(27) D. Craig, *J. Amer. Chem. Soc.*, **55**, 3723 (1933).

tion, utilizing halogen substituents as blocking groups. Condensation of 3-bromo-9-ethylcarbazole (**7c**) (Scheme I) or 3-iodo-9-ethylcarbazole (**7d**) with formaldehyde in acetic acid yielded bis(6-bromo-9-ethyl-3-carbazolyl)methane (**8c**) or bis(6-iodo-9-ethyl-3-carbazolyl)methane (**8d**), respectively, as homogeneous crystalline materials. Reductive dehalogenation of either the bisbromo compound by means of the lithium-*t*-butyl alcohol-tetrahydrofuran procedure<sup>28</sup> or of the bisiodo compound by reduction with lithium aluminum hydride in ether afforded bis(9-ethyl-3-carbazolyl)methane (**3c**), mp 143°. A similar reaction sequence starting with 3-iodo-9-methylcarbazole (**7e**) yielded bis(6-iodo-9-methyl-3-carbazolyl)methane (**8e**) and thence, by LiAlH<sub>4</sub>-ether reduction, bis(9-methyl-3-carbazolyl)methane (**3b**), mp 191°. The infrared and nmr spectra of these products and of the intermediate compounds were in perfect agreement with the required structures. After our study was completed Traven, Plakhov, and Stepanov<sup>18c</sup> isolated a product, mp 223°, from the direct 9-methylcarbazole-formaldehyde condensation reaction, which they designated as bis(9-methyl-3-carbazolyl)methane, and Nakade, Funayama, and Gomi<sup>20</sup> obtained a material from the corresponding 9-ethylcarbazole-formaldehyde reaction which they claimed to be bis(9-ethyl-3-carbazolyl)methane, mp 183–186°. In the light of the foregoing discussion and previous literature<sup>12,26</sup> commenting on the nonhomogeneous, resinous nature of the products from such reactions, and in view of the melting point discrepancies, when compared with our materials, we conjecture that these products are, in fact, higher oligomeric species, *e.g.*, **10**, **13**, etc.

As stated above, the condensation reaction may be visualized as proceeding *via* the initial formation of a 3-hydroxymethylcarbazole intermediate, *e.g.*, **11**, formed *in situ*. In the case of the carbazoles containing nuclear blocking substituents, it was felt that the intermediate bis(6-halogeno-9-alkyl-3-carbazolyl)methanes **8** would also be accessible by direct condensation of the appropriate 6-halogeno-3-hydroxymethylcarbazole **14** with the corresponding 3-halogeno-9-alkylcarbazole, *e.g.*

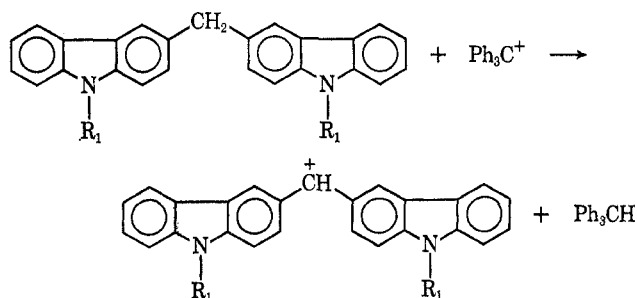


Mild acid treatment of an equimolar mixture of 3-hydroxymethyl-6-bromo-9-ethylcarbazole (**14**) and 3-bromo-9-ethylcarbazole (**7c**) afforded bis(6-bromo-9-ethyl-3-carbazolyl)methane (**8c**), identical in all respects with the material obtained from the direct 3-bromo-9-ethylcarbazole-formaldehyde condensation. The intermediate 3-hydroxymethyl-6-bromo-9-ethylcarbazole (**14**) was easily accessible from the sodium borohydride reduction of 6-bromo-9-ethylcarbazole-3-carboxaldehyde (**4g**).

Finally the alkylated biscarbazolylmethanes **3b** and **3c** may also be obtained (Scheme I) by N-alkylation of the parent bis(3-carbazolyl)methane **3a**, the synthesis of which is reported above. Ethylation of this

material with diethyl sulfate in acetone<sup>29</sup> afforded bis(9-ethyl-3-carbazolyl)methane (**3c**) in moderate yield, the product being identical in all respects with the material obtained from the dehalogenations of bis(6-bromo-9-ethyl-3-carbazolyl)methane (**8c**) and bis(6-iodo-9-ethyl-3-carbazolyl)methane (**8d**). Similarly, methylation of bis(3-carbazolyl)methane with dimethyl sulfate afforded bis(9-methyl-3-carbazolyl)methane (**3b**), identical with the product from LiAlH<sub>4</sub>-ether reduction of bis(6-iodo-9-methyl-3-carbazolyl)methane (**8e**).

As leuco derivatives analogous to 4,4'-diaminodiphenylmethane derivatives **1**, the bis(3-carbazolyl)methanes were good color formers (yielding blue dyes) with hydride abstractors such as tropylium fluoroborate or trityl hexachloroantimonate.<sup>30</sup> The kinetics of



such color-forming reactions will be described in a second forthcoming paper.<sup>31</sup>

### Experimental Section

Melting points were taken on a Fisher-Johns melting point apparatus in most cases; compounds which melted above 280° or which sublimed at atmospheric pressure were examined in sealed capillaries in an electrothermal melting point apparatus, the cavity temperature of which was monitored with a chromel-alumel thermocouple. Infrared spectra were run in potassium bromide pellets on a Perkin-Elmer Model 21 double beam spectrophotometer. <sup>1</sup>H nmr spectra were obtained on a Varian Associates A60-A spectrometer utilizing various solvents. Chemical shifts are in  $\delta$  values downfield from the standard tetramethylsilane ( $\delta$  0) position. Microanalyses were performed by Elek Microanalytical Laboratories, Torrance, Calif.

**Materials.**—Carbazole was J. T. Baker practical grade, recrystallized from 2-propanol; 9-ethylcarbazole was obtained from the Aldrich Chemical Co. and was recrystallized from methanol. Pyridine was dried over potassium hydroxide pellets, decanted, and redistilled from fresh pellets. Tetrahydrofuran and diethyl ether were dried by distillation from lithium aluminum hydride. The following compounds were prepared according to the cited literature references: 9-hydroxymethylcarbazole<sup>9</sup> (**4a**), mp 128–129° (lit.<sup>9</sup> 127–128°); 9-acetoxymethylcarbazole<sup>14b</sup> (**4b**), mp 80–82° (lit.<sup>14b</sup> 81–82°); 3-iodocarbazole,<sup>32</sup> mp 194–196° (lit.<sup>32</sup> 192–194°); 3-iodo-9-methylcarbazole<sup>29</sup> (**7e**), mp 78–79° (lit.<sup>29</sup> 77–79°); 3-iodo-9-ethylcarbazole<sup>32</sup> (**7d**), mp 82–83° (lit.<sup>32</sup> 83–84°); 3,6-diiodocarbazole<sup>32</sup> (**4e**), mp 206–207° (lit.<sup>32</sup> 202–204°); 3-bromo-9-ethylcarbazole<sup>32</sup> (**7c**), mp 81–82° (lit.<sup>32</sup> 81–82°); 4,4'-dihydrazinodiphenylmethane,<sup>33,34</sup> mp 139–141° (lit.<sup>33b</sup> 141–143°) (previous workers<sup>33,34</sup> prepared this hydrazine by reduction of the intermediate diphenylmethane-4,4'-tetrazonium dichloride with sodium sulfite, but we found the general method

(29) T. S. Stevens and S. H. Tucker, *J. Chem. Soc.*, **123**, 2140 (1923).

(30) A. Ledwith, A. M. North, and K. E. Whitelock, *Eur. Polym. J.*, **4**, 133 (1967).

(31) P. Bruck, A. Ledwith, and A. C. White, *J. Chem. Soc. B*, in press.

(32) S. H. Tucker, *J. Chem. Soc.*, 547 (1926).

(33) R. H. Meen and H. Gilman, *J. Org. Chem.*, **20**, 73 (1955).

(34) (a) H. Finger, *J. Prakt. Chem.*, **74**, 155 (1906); (b) G. D. Parkes and R. H. H. Morley, *J. Chem. Soc.*, 315 (1936).

(28) P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind. (London)*, 405 (1960).

of Hunsberger, *et al.*,<sup>35</sup> utilizing stannous chloride, to be more convenient); 9-ethylcarbazole-3-carboxaldehyde<sup>36,37</sup> (4f), mp 89–91° (lit.<sup>36</sup> 94°).

**Bis(3,6-diiodo-9-carbazolyl)methane (5d).**—Methylal (0.7 g) and 4e (6.2 g) were dissolved in acetic acid (110 ml). At 65–70°, 1 ml of a 4% solution (v/v) of sulfuric acid in acetic acid was added. An immediate white precipitate formed. The collected product, which was almost insoluble in most of the conventional organic solvents, recrystallized from a large volume of boiling anisole as felted needles: mp 314–316° dec, ir (KBr) 805 cm<sup>-1</sup> (1,2,4-trisubstituted benzene ring).

*Anal.* Calcd for C<sub>26</sub>H<sub>18</sub>N<sub>2</sub>I<sub>2</sub>: C, 35.32; H, 1.66; N, 3.30. Found: C, 35.18; H, 1.72; N, 3.56.

**Bis(9-carbazolyl)methane (5a).** (A) **From Lithium Aluminum Hydride Reductive Deiodination of 5d.**—The difficultly soluble 5d (3.4 g) was extracted for 4 days in a Soxhlet apparatus with tetrahydrofuran (150 ml) containing lithium aluminum hydride (3 g). During this time, 1 g of 5d dissolved. The solution was treated with saturated ammonium chloride solution and then with 2 N HCl (200 ml) to dissolve inorganic salts. After further dilution with H<sub>2</sub>O, the resultant precipitate was dissolved in hot benzene (200 ml), filtered, and concentrated to 50 ml. Fine white crystalline needles of 5a (0.271 g), mp 314–315° (lit.<sup>14a</sup> 313–314°), were obtained.

(B) **From the Reaction of 9-Carbazolylmagnesium Iodide with 9-Acetoxyethylcarbazole (4b).**—This experiment followed the procedure given by Mizuch.<sup>14a</sup> The resultant product was recrystallized from N,N-dimethylformamide and afforded 5a, mp 314–316° (lit.<sup>14a</sup> 313–314°).

*Anal.* Calcd for C<sub>26</sub>H<sub>18</sub>N<sub>2</sub>: C, 86.67; H, 5.24; N, 8.09. Found: C, 86.70; H, 5.20; N, 7.97.

(C) **From Condensation of Carbazole and Formaldehyde.**—The procedure of Feldman and Wagner<sup>13</sup> was followed. The crude reaction product was recrystallized from N,N-dimethylformamide and then sublimed at 280° (0.15 mm), yielding 5a, mp 315–317° (lit. "above 280",<sup>4,6</sup> 287,<sup>10</sup> 301–303,<sup>13</sup> 313–314°<sup>14a</sup>).

(D) **From Condensation of Carbazole and Methylal.**—The preparation of the biscarbazolylmethane *via* this route was mentioned by Votocek and Vesely,<sup>9</sup> but with no experimental details. A solution of carbazole (17.7 g) in acetic acid (350 ml) was refluxed while a solution of methylal (3.8 g) in acetic acid (20 ml) was added. The resultant crystalline product was recrystallized from N,N-dimethylformamide and afforded 5a, mp 316–317°.

*Anal.* Calcd for C<sub>26</sub>H<sub>18</sub>N<sub>2</sub>: C, 86.67; H, 5.24; N, 8.09. Found: C, 86.99; H, 5.37; N, 8.21.

(E) **From 9-Hydroxymethylcarbazole.**—The preparation of a biscarbazolylmethane from 4a in acid medium was described by Lange,<sup>9</sup> but with no experimental details. A solution of 4a (2.5 g) in acetic acid (25 ml) was warmed to 90° and held at this temperature for 30 min. The resultant crystalline precipitate of 5a was collected, washed with acetone, and dried *in vacuo*, mp 315–317°.

The products from steps A–E were taken in various combinations for mixture melting point determinations. No depressions were observed. The infrared spectra were superimposable and were noteworthy for the complete absence of the NH absorption in the 3300–3500-cm<sup>-1</sup> range; ir (KBr) 3030 (aromatic CH), 1460 (CH<sub>2</sub>), 1120, 745, and 720 cm<sup>-1</sup> (1,2-substituted benzene ring). The integrated <sup>1</sup>H nmr spectrum (CH<sub>3</sub>CONMe<sub>2</sub> at 120°) showed absorptions corresponding to 16 aromatic protons and 2 methylene protons (for details, see text).

**Bis(5,6,7,8-tetrahydro-3-carbazolyl)methane(6).**—This compound was prepared from cyclohexanone and 4,4'-dihydrazinodiphenylmethane by the method of Borsche and Kienitz.<sup>23a</sup> The crude tetrahydrocarbazole was recrystallized from acetone, mp 281–283° (lit. 265,<sup>23a</sup> 281–283°<sup>23b</sup>); ir (KBr) 3400 (NH), 2940 (CH<sub>2</sub>), 880, and 795 cm<sup>-1</sup> (1,2,4-trisubstituted benzene ring); nmr (DMSO-*d*<sub>6</sub>) δ 6.7–7.2 (m, 6 H, aromatic protons), 4.0 (s, 2 H, methylene group), 2.6 (m, 4 H, aliphatic protons), and 1.8 (m, 4 H, aliphatic protons).

**Bis(3-carbazolyl)methane (3a).**—An intimate mixture of palladium on charcoal (1.2 g) and 6 (3.6 g) was heated in a stream of nitrogen (Woods metal bath). A vigorous evolution of gaseous products occurred at approximately 250°. The reaction mix-

ture was cooled and extracted twice with hot xylene; the combined xylene extracts were filtered. The product (1.3 g) crystallized as large off-white nacreous plates, mp 350–352°; ir (KBr) 3300 (NH), 800 (1,2,4-trisubstituted benzene ring), 750, and 725 cm<sup>-1</sup> (1,2-disubstituted benzene ring); nmr (DMSO) δ 9.7 (2 H, NH), 7.7 (d, 4 H, 4 and 5 aromatic protons), 6.5–7.3 (m, 10 H, aromatic protons), and 3.9 (s, 2 H, CH<sub>2</sub>).

*Anal.* Calcd for C<sub>25</sub>H<sub>18</sub>N<sub>2</sub>: C, 86.67; H, 5.24; N, 8.09. Found: C, 86.72; H, 5.19; N, 8.10.

**6-Bromo-9-ethylcarbazole-3-carboxaldehyde (4g).**—This material had previously been obtained<sup>36</sup> by bromination of 4f. We found dimethylformamide-phosphorous oxychloride formylation of 7c to be equally convenient.

Dimethylformamide (2.5 g) and 7c (8.2 g) were dissolved in *o*-dichlorobenzene (20 ml) and POCl<sub>3</sub> (4.6 g) was added. The red-brown mixture, after being heated for 4 hr at 90–100°, was cooled, poured into H<sub>2</sub>O, and extracted with ether. The ethereal extract was washed with H<sub>2</sub>O, dried (K<sub>2</sub>CO<sub>3</sub>), filtered, and evaporated. The oily residue crystallized from ethanol at 0° as fine pale yellow needles, mp 133–134° (lit.<sup>36</sup> 136°).

**3-Hydroxymethyl-9-ethylcarbazole (11).**—A solution of 4f (5.5 g) in methanol–2% sodium hydroxide was treated with sodium borohydride (0.5 g). After being allowed to stand overnight at room temperature, the solution was diluted with H<sub>2</sub>O and extracted with benzene. The benzene extract was dried, filtered, and evaporated. The residue crystallized from ethanol at –10° as felted needles, mp 75–76° (3.8 g); nmr (CDCl<sub>3</sub>) δ 7.8 (m, 2 H, 4 and 5 carbazole protons), 6.9–7.3 (m, 5 H, remaining aromatic protons), 4.6 (s, 2 H, CH<sub>2</sub>OH), 4.1 (q, 2H, N-CH<sub>2</sub>CH<sub>3</sub>, *J* = 7 cps), 2.5 (s, 1 H, OH), and 1.2 (t, 3 H, N-CH<sub>2</sub>CH<sub>3</sub>).

*Anal.* Calcd for C<sub>15</sub>H<sub>15</sub>NO: C, 79.97; H, 6.71. Found: C, 80.02; H, 6.70.

**3-Hydroxymethyl-6-bromo-9-ethylcarbazole (14).**—In a similar reduction to the above, 4g (1.7 g) was refluxed for 6 hr with NaBH<sub>4</sub> (3 g) in methanol (50 ml) containing KOH (1 g). After cooling, unchanged aldehyde was removed by filtration and the filtrate was diluted with H<sub>2</sub>O. The collected product was crystallized from carbon tetrachloride and then from benzene as transparent spars, mp 143–144° (0.63 g); nmr (CDCl<sub>3</sub>) δ 8.1 (d, 1 H, 5 proton), 7.9 (s, 1 H, 4 proton), 4.7 (s, 2 H, CH<sub>2</sub>OH), 4.2 (q, 2 H, N-CH<sub>2</sub>CH<sub>3</sub>), 2.0 (s, 1 H, OH), and 1.3 (t, 3 H, N-CH<sub>2</sub>CH<sub>3</sub>).

*Anal.* Calcd for C<sub>15</sub>H<sub>14</sub>BrNO: C, 59.22; H, 4.64; N, 4.60. Found: C, 59.17; H, 4.59; N, 4.68.

**Bis(6-bromo-9-ethyl-3-carbazolyl)methane (8c).** (A) **From 3-Bromo-9-ethylcarbazole and Formaldehyde.**—A solution of 7c (27.4 g) in a mixture of glacial acetic acid (100 ml) and sulfuric acid (2 ml) was warmed to 85° with stirring. At this temperature 37% formalin solution (4.1 ml) in acetic acid (10 ml) was added at once. A greenish blue precipitate formed. The collected material was taken in hot benzene and acetone was added dropwise until solution was completed; the solution was then treated twice with charcoal. The resultant wine red filtrate deposited crystalline needles, mp 185–188° (13 g, 45%). Two recrystallizations of this material from benzene afforded 8c, mp 193–194°; nmr (CDCl<sub>3</sub>) δ 8.1 (d, 2 H, 5 protons), 7.8 (s, 2 H, 4 protons), 7.0–7.5 (m, 8 H, remaining aromatic protons), 4.3 (s, 2 H, Ar-CH<sub>2</sub>-Ar), 4.2 (q, 4 H, N-CH<sub>2</sub>CH<sub>3</sub>), and 1.3 (t, 6 H, N-CH<sub>2</sub>CH<sub>3</sub>).

*Anal.* Calcd for C<sub>28</sub>H<sub>24</sub>Br<sub>2</sub>N<sub>2</sub>: C, 62.16; H, 4.32; N, 5.00. Found: C, 62.72; H, 4.61; N, 5.01.

(B) **From 3-Hydroxymethyl-6-bromo-9-ethylcarbazole and 3-Bromo-9-ethylcarbazole.**—A solution of 7c (100 mg) and 14 (100 mg) in acetic acid (3 ml) was treated with one drop of a solution made by adding sulfuric acid (2 drops) to acetic acid (10 ml). The solution was boiled for 3 min, cooled, diluted with H<sub>2</sub>O dropwise until turbid, and then allowed to stand. The resultant product was crystallized from benzene (2 ml) and yielded 40 mg, mp 193–194°, undepressed in melting point upon admixture with the product obtained from route A above.

**Bis(6-iodo-9-ethyl-3-carbazolyl)methane (8d).**—A suspension of 7d (16.0 g) in a solution of 50% aqueous sulfuric acid (2 ml) in acetic acid (75 ml) was treated with a solution of methylal (1.9 g) in acetic acid (10 ml). The mixture was stirred and heated under reflux; the iodocarbazole passed into solution and subsequently a blue precipitate appeared. The product was filtered, taken in benzene (500 ml), and treated twice with charcoal. The pale green filtrate was treated with piperidine (2 drops) and the resultant yellow solution was concentrated to 75 ml and allowed to stand at room temperature. The resultant pinkish needles

(35) I. M. Hunsberger, E. R. Shaw, J. Fugger, R. Ketcham, and D. Ledner, *J. Org. Chem.*, **21**, 394 (1956).

(36) Ng. P. Buu-Hoi and Ng. Hoan, *ibid.*, **16**, 1327 (1951).

(37) L. Burgardt, E. Reckziegel, and O. Wahl, German Patent 950,617 (1956).

were recrystallized from benzene and afforded **8d**, mp 204–205° (6.4 g).

*Anal.* Calcd for  $C_{29}H_{24}I_2N_2$ : C, 53.23; H, 3.70; N, 4.16. Found: C, 53.22; H, 3.91; N, 4.28.

**Bis(6-iodo-9-methyl-3-carbazolyl)methane (8e).**—In a similar experiment to the one above, **7e** (9.2 g) was treated with methylal (1.3 g) in refluxing acetic acid. The mixture was worked up as above and the reaction product was recrystallized from benzene, yielding **8e**, mp 249–252° (5.7 g).

*Anal.* Calcd for  $C_{27}H_{20}I_2N_2$ : C, 51.77; H, 3.22; N, 4.47. Found: C, 51.54; H, 3.18; N, 4.40.

**Bis(9-ethyl-3-carbazolyl)methane (3c).** (A) **From Lithium-*t*-Butyl Alcohol-Tetrahydrofuran Dehalogenation of 8c.**—A solution of **8c** (5.6 g) in a mixture of dry tetrahydrofuran (50 ml) and *t*-butyl alcohol (3 g) was stirred under a nitrogen atmosphere while lithium shot (0.7 g) was added, followed by methyl iodide (5 drops). The mixture was refluxed for 2 hr and was then poured onto crushed ice. After the excess lithium had decomposed, the mixture was acidified with 2 *N* HCl and extracted with ether (two 100-ml portions). The ether extract was washed with  $H_2O$ , dried ( $K_2CO_3$ ), filtered, and evaporated. The yellow oily residue was chromatographed on alumina (Woelm, basic, activity grade 1), utilizing petroleum ether (bp 30–40°) as initial eluent. This solvent removed an oily product (0.4 g), which was not investigated. The major product was subsequently eluted with petroleum ether–5% ether. Crystallization of this material from ether afforded **3c**, mp 143–144°, as shimmering flakes; ir (KBr) 2940 ( $CH_3$ ), 800 (1,2,4-trisubstituted benzene ring), and 750 and 725  $cm^{-1}$  (1,2-disubstituted benzene ring); nmr ( $CDCl_3$ )  $\delta$  8.0 (d, 4 H, 4 and 5 protons), 6.8–7.4 (m, 10 H, aromatic protons), 4.3 (q, 4 H,  $N-CH_2CH_3$ ), 4.3 (s, 2 H,  $Ar-CH_2-Ar$ ), and 1.4 (t, 6 H,  $N-CH_2CH_3$ ).

*Anal.* Calcd for  $C_{28}H_{26}N_2$ : C, 86.53; H, 6.51; N, 6.96. Found: C, 86.37; H, 6.47; N, 7.25.

If crystallization of the product was attempted from benzene-ether mixtures, a form apparently containing benzene of crystallization, mp 109–110°, was obtained. The solvent of crystallization could be driven off by holding the liquid melt at 120–125°; the residue then solidified and finally melted at 142–143°.

(B) **From Lithium Aluminum Hydride Reduction of 8d.**—A solution of **8d** (1.07 g) in tetrahydrofuran (50 ml) containing  $LiAlH_4$  (1 g) was refluxed overnight. After destruction of excess hydride with ethyl acetate, benzene (100 ml) was added and the mixture was treated with 2 *N* HCl (100 ml). The organic layer was separated, washed with  $H_2O$  (three 50-ml portions), dried ( $Na_2SO_4$ ), filtered, and evaporated to dryness. The residue (406 mg) was crystallized twice from ether and afforded **3c**, mp 142–143° (undepressed upon admixture with the material obtained from route A above).

(C) **From Ethylation of 3a.**—A suspension of **3a** (420 mg) in acetone (75 ml) was treated with a solution of sodium hydroxide (2.5 g) in water (3 ml), followed by diethyl sulfate (6 ml). The mixture was stirred and refluxed for 4 hr and filtered (much unchanged bis(3-carbazolyl)methane was recovered), and the fil-

trate was diluted with  $H_2O$ . The product was extracted into ether and the ether extract was washed with water, dried ( $K_2CO_3$ ), filtered and concentrated to approximately 2 ml volume. Crystalline plates of **3c** (73 mg) were obtained, mp 139–140°, mixture melting point with material prepared by debromination of bis(6-bromo-9-ethyl-3-carbazolyl)methane, 140–142°.

**Bis(9-methyl-3-carbazolyl)methane (3b).** (A) **From Lithium Aluminum Hydride Reduction of 9e.**—Bis(6-iodo-9-methyl-3-carbazolyl)methane (2.9 g) was reduced with lithium aluminum hydride (1.4 g) in tetrahydrofuran (100 ml) in a similar manner to the treatment of the 9-ethyl compound above. The resultant product was recrystallized from ether and afforded **3b**, mp 190–191° (0.95 g); nmr ( $CDCl_3$ )  $\delta$  8.0 (d, 4 H, 4 and 5 protons), 6.8–7.5 (m, 10 H, remaining aromatic protons), 4.3 (s, 2 H,  $Ar-CH_2-Ar$ ), and 3.7 (s, 6 H,  $N-CH_3$ ).

*Anal.* Calcd for  $C_{27}H_{22}N_2$ : C, 86.59; H, 5.92; N, 7.48. Found: C, 86.42; H, 6.03; N, 7.42%.

(B) **From Methylation of 3a.**—A suspension of **3a** (720 mg) in acetone (100 ml) containing potassium hydroxide (3 g) and water (4 ml) was treated, at the reflux point, with dimethyl sulfate (10 ml). The mixture was stirred and refluxed for 4 hr and was then worked up in the manner of the corresponding ethylation reaction above. The yield of bis(9-methyl-3-carbazolyl)methane, mp 191–192°, was 183 mg (25%).

**Condensation of 9-Ethylcarbazole with Formaldehyde.**—A solution of ethylcarbazole (4.9 g; 0.025 mol) in acetic acid (100 ml) containing sulfuric acid (0.2 g) was heated to 85° and a solution of formaldehyde (0.013 mol) in acetic acid (11 ml) was added dropwise at this temperature. After addition was complete, the mixture was refluxed for 5 min, then poured into xylene (650 ml), and the acetic acid removed by distillation. The resultant blue xylene solution was evaporated to small bulk and treated with piperidine (2 drops); the resultant pale yellow solution was filtered. The product was obtained at 0° as pale buff microcrystalline prisms, which partly melted in the range 190–200°, but did not melt further up to 270°; mol wt 1649, 1784; ir (KBr) 804 (1,2,4-trisubstituted benzene rings) and 735 and 750  $cm^{-1}$  (weak only, 1,2-disubstituted benzene ring, carbazole end group).

**Self-Condensation of 11.**—A cold solution of **11** (8 g) in acetic acid (25 ml) was added to a second portion of acetic acid (75 ml) held at 90–95°; a bluish white precipitate appeared. The collected product was dissolved in tetrahydrofuran and poured into an excess of sodium bicarbonate solution. The resultant white product (4.7 g) had mp 163–164°, with prior softening at 157°; mol wt 1699, 1775, 1756; ir (KBr) 3400 (OH), 800 (1,2,4-trisubstituted benzene ring), and 735 and 750  $cm^{-1}$  (weak only, 1,2-disubstituted benzene ring, carbazole end group).

**Registry No.**—**3a**, 24290-44-6; **3b**, 18152-70-0; **3c**, 16391-67-6; **4g**, 24301-72-2; **5a**, 6510-63-0; **5d**, 24301-74-4; **6**, 24301-75-5; **8c**, 24301-76-6; **8d**, 24301-77-7; **8e**, 24301-78-8; **11**, 24301-79-9; **14**, 24301-80-2.