

## Reactions of a Methyl and Bromomethyl Side Chain

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Enhanced reactivity of the methyl group of 2-*t*-butyl-5-methyl-1,3,4,6,9b-pentaazaphenalene allowed acetic anhydride-catalyzed condensation reactions with several aromatic aldehydes, and base-catalyzed alkylation reactions with several alkyl halides to take place, albeit in low yields. Of the many nucleophiles tried, only salts of carboxylic acids, in the presence of 18-crown-6, were able to displace bromine from 2-(bromomethyl)-5-methyl-1,3,4,6,9b-pentaazaphenalene.

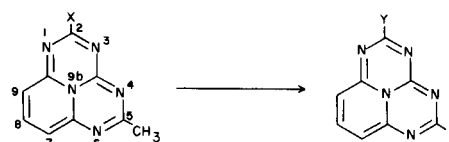
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It is often observed that a methyl group, when attached to the alpha position of certain nitrogen heterocycles such as pyridine or quinoline, shows increased reactivity to condensation (2), alkylation (2), oxidation (3), and halogenation (4) reactions. It was of interest to determine if this enhanced reactivity would be allowed in suitable methyl derivatives of the 1,3,5,6,9b-pentaazaphenalene ring system.

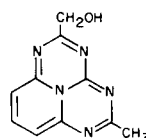
Our initial condensation studies involved the acetic anhydride-catalyzed reaction of benzaldehyde with the readily available 2,5-dimethyl-1,3,4,6,9b-pentaazaphenalene (**1**) (5). Both 2,5-bis(2-phenylethenyl)-1,3,4,6,9b-pentaazaphenalene (**4**) and 2-methyl-5-(2-phenylethenyl)-1,3,4,6,9b-pentaazaphenalene (**5**) were obtained in 22 and 17% yields, respectively, after a 17 hour reflux, even though the molar ratio of benzaldehyde/**1** was three. Subsequent study showed that a mixture of products would result regardless of the molar concentration of the reactants. To avoid this problem, we prepared 2-*t*-butyl-5-methyl-1,3,4,6,9b-pentaazaphenalene (**2**) using a synthetic route developed previously (5). Thus reaction of *N*-cyano-*N'*-(6-amino-2-pyridyl)acetamide (**18**) with trimethylacetyl chloride in the presence of pyridine gave **2** in 39% yield. This monomethyl derivative also had much improved solubility characteristics in the reaction solvents employed; it was used in all of the subsequent condensation and alkylation studies. The reaction of **2** with benzaldehyde, *p*-nitrobenzaldehyde, *p*-tolualdehyde, *p*-dimethylaminobenzaldehyde, and terephthaldicarboxaldehyde was carried out under reaction conditions similar to those just described for **1** (except in the case of terephthaldicarboxaldehyde, where a slight excess of **2** was used). The desired condensation products (**6-9**) were obtained in moderate yield except in the case of *p*-tolualdehyde and *p*-dimethylaminobenzaldehyde where the yields were 9 and 0%, respectively.

Alkylation of **2** with methyl iodide, propyl bromide, hexyl bromide and benzyl chloride was achieved in 9, 12, 8, and 10% yields, respectively, by treating a solution of **2** in *N,N*-dimethylformamide with an equimolar portion of

Figure 1



- 1, X = CH<sub>3</sub>  
2, X = (CH<sub>3</sub>)<sub>3</sub>C  
3, X = CH<sub>2</sub>Br



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- 4, Y = Z, Z = CH=CHC<sub>6</sub>H<sub>5</sub>  
5, Y = CH<sub>3</sub>, Z = CH=CHC<sub>6</sub>H<sub>5</sub>  
6, Y = (CH<sub>3</sub>)<sub>3</sub>C, Z = CH=CHC<sub>6</sub>H<sub>5</sub>  
7, Y = (CH<sub>3</sub>)<sub>3</sub>C, Z = CH=CH-*p*-C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>  
8, Y = (CH<sub>3</sub>)<sub>3</sub>C, Z = CH=CH-*p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>  
9, Y = (CH<sub>3</sub>)<sub>3</sub>C, Z = CH=CH-*p*-C<sub>6</sub>H<sub>4</sub>-C<sub>14</sub>H<sub>14</sub>N<sub>5</sub>  
10, Y = (CH<sub>3</sub>)<sub>3</sub>C, Z = CH<sub>2</sub>CH<sub>3</sub>  
11, Y = (CH<sub>3</sub>)<sub>3</sub>C, Z = (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>  
12, Y = (CH<sub>3</sub>)<sub>3</sub>C, Z = (CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub>  
13, Y = (CH<sub>3</sub>)<sub>3</sub>C, Z = CH(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>  
14, Y = O(CO)H, Z = CH<sub>3</sub>  
15, Y = O(CO)CH<sub>3</sub>, Z = CH<sub>3</sub>  
16, Y = O(CO)C<sub>6</sub>H<sub>5</sub>, Z = CH<sub>3</sub>

sodium hydride followed by addition of excess alkyl halide. The reactions were accompanied by considerable tar formation and polyalkylation. Indeed, in the case of benzyl chloride, only the dialkylated product could be isolated in pure form. The other alkyl halides gave characterizable monalkylated products but were accompanied by inseparable mixtures of higher alkylated products.

Attempted acylation of **2** by substitution of methyl benzoate, carbon dioxide (dry ice) or ethyl formate in the alkylation procedure just described was not successful.

Oxidation of **2** by selenium dioxide or a potassium permanganate complex with dicyclohexyl-18-crown-6 resulted in complete destruction of the ring system.

Unsuccessful efforts to introduce halogen into the methyl side chain of **1** (under conditions usually rather favorable to this end, *i.e.*, *N*-bromosuccinimide, heat, light) were reported in a previous paper (6); bromination at position-7 of **1** occurred instead. However, the desired 2-(bromomethyl)-5-methyl-1,3,4,6,9b-pentaazaphenalene (**3**) (**6**) was obtained by reaction of bromoacetyl bromide

with **18** in the presence of pyridine.

Displacement reactions of **3** with various nucleophiles have since been investigated and for the most part **3** has been found to be very reluctant to undergo such reactions. Thus the following nucleophile/solvent combinations (refluxing solvent), resulted either in the formation of intractable tars (T) or no reaction (NR): sodium methoxide/methanol (T); silver nitrate/methanol (NR); potassium acetate/acetone (NR); silver acetate/acetic acid (NR); potassium cyanide/2-methoxyethanol-water (T); potassium cyanide/18-crown-6-acetonitrile (T); sodium azide/acetone-water (T); sodium azide/18-crown-6-acetonitrile (T); pyrrolidine/acetonitrile (T). The only successful displacement reactions found were reactions of salts of carboxylic acids with **3** in the presence of 18-crown-6, in refluxing acetonitrile. Thus the reaction of **3** with sodium formate, potassium acetate or potassium benzoate, under these conditions, gave 2-formyloxymethyl-5-methyl-1,3,4,6,9b-pentaazaphenalene (**14**), 2-acetyloxymethyl-5-methyl-1,3,4,6,9b-pentaazaphenalene (**15**), and 2-benzoyloxymethyl-5-methyl-1,3,4,6,9b-pentaazaphenalene (**16**), in 37, 51, and 18% yields, respectively. In the absence of 18-crown-6, the same reagents and reaction conditions gave no reaction with **3**. This increased nucleophilicity of potassium and sodium salts of carboxylic acids in the presence of 18-crown-6/acetonitrile has been noted by Liotta and Grisdale (7).

The room temperature reaction of **14** with pyrrolidine in chloroform resulted in the formation of 2-hydroxymethyl-5-methyl-1,3,4,6,9b-pentaazaphenalene (**17**), in 19% yield. Attempted oxidation of **17** to the corresponding aldehyde using chromic anhydride.2 pyridine (Sarett's reagent) in methylene chloride, or dimethylsulfoxide/dicyclohexylcarbodiimide in ethyl acetate led to intractable tars.

## EXPERIMENTAL

Melting points were determined in open capillaries on a Thomas-Hoover melting point bath and are uncorrected. Infrared spectra were recorded using a Perkin-Elmer 735B spectrophotometer. Pmr spectra were determined on a Varian EM-360 spectrometer using TMS as an internal reference. Analyses were performed by Micro-Analysis Inc., Wilmington, Delaware. All evaporations were carried out on a rotary evaporator at reduced pressure.

*N,N*-Dimethylformamide (DMF), 1,2-dimethoxyethane (glyme), acetonitrile, and pyridine were dried using standard methods and stored over molecular sieves. The following compounds were obtained from Aldrich Chemical Company and used without further purification: 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6), sodium hydride (50% dispersion in mineral oil), *p*-nitrobenzaldehyde, *p*-tolualdehyde, terephthaldicarboxaldehyde, trimethylacetyl chloride and hexyl bromide. Woelm silica gel (70-230 mesh) for column chromatography was obtained from ICN Pharmaceutical Inc. 2,5-Dimethyl-1,3,4,6,9b-pentaazaphenalene **1** (5), *N*-cyano-*N'*-(6-amino-2-pyridyl)acetamidine **18** (5), and 2-(bromomethyl)-5-methyl-1,3,4,6,9b-pentaazaphenalene **3** (6) were prepared using methods described in the literature.

2,5-Bis(2-phenylethenyl)-1,3,4,6,9b-pentaazaphenalene (**4**) and 2-Methyl-5-(2-phenylethenyl)-1,3,4,6,9b-pentaazaphenalene (5).

A mixture of 1.99 g. (0.01 mole) of **1** and 3.18 g. (0.03 mole) of benzaldehyde and 10 ml. of acetic anhydride was refluxed for 17 hours. The precipitate that formed on cooling to room temperature was filtered, washed with ether and recrystallized from 25 ml. of chlorobenzene. The filtrate "A" from this recrystallization was set aside for further work-up. The ether-washed filter cake of crude **4** weighed 0.83 g. (22%), m.p. 275-281°. An additional recrystallization from chlorobenzene gave green crystals, m.p. 282-284°; pmr (deuteriochloroform):  $\delta$  6.1 [d (J = 8 Hz), 2H, H-7 and H<sub>9</sub>], 6.57 [d (s = 16 Hz), 1H, C=CH], 7.04-7.69 (m, 11H, phenyl-H and H-8), 7.94 [d (J = 16 Hz), 1H, C=CH].

Anal. Calcd. for C<sub>22</sub>H<sub>17</sub>N<sub>5</sub> (**4**): C, 76.78; H, 4.57; N, 18.66. Found: C, 76.71; H, 4.44; N, 18.39.

Filtrate "A" was evaporated to dryness and the residue was dissolved in 5 ml. of chloroform and chromatographed on 40 g. of silica using chloroform as eluent. Collection of a purple fraction yielded 0.48 g. (17%) of **5**, m.p. 234-236°. Recrystallization from chlorobenzene gave purple needles, m.p. 238-240°; pmr (deuteriochloroform):  $\delta$  2.05 (s, 3H, CH<sub>3</sub>), 6.1 (m, 2H, H<sub>7</sub> and H<sub>9</sub>), 6.45 [d (J = 16 Hz), 1H, C=CH], 7.09-7.65 (m, 6H, phenyl-H and H-8), 7.9 [d (J = 16 Hz), 1H, C=CH].

Anal. Calcd. for C<sub>17</sub>H<sub>13</sub>N<sub>5</sub> (**5**): C, 71.06; H, 4.56; N, 24.38. Found: C, 70.95; H, 4.32; N, 24.17.

2-*t*-Butyl-5-methyl-1,3,4,6,9b-pentaazaphenalene (**2**).

A cold (8°) stirred slurry of 26.3 g. (0.15 mole) of **18**, 11.9 g. (0.15 mole) of dry pyridine and 200 ml. of dry glyme (nitrogen atmosphere) was treated dropwise with 43.4 g. (0.36 mole) of trimethylacetyl chloride while maintaining the temperature at or slightly below 8° during the addition. The thick reaction mixture was then stirred and gently refluxed for 24 hours, cooled to room temperature, filtered and the filter cake was washed with ether. An ice-cold stirred slurry of the reaction product in 90 ml. of methanol was carefully neutralized to ~ pH 10 by the slow addition of 1*N* methanolic sodium methoxide. The residue obtained by filtration of this slurry and evaporation of the filtrate to dryness, was taken up in 250 ml. of chloroform, filtered and the filtrate was evaporated to dryness. Filtration of the combined chilled extracts obtained by boiling this residue with 6 x 350 ml. portions of petroleum ether (110-120°) gave 14.2 g. (39%) of **2**, m.p. 193-195°. Recrystallization from petroleum ether (110-120°) gave a red fluffy solid, m.p. 196-198°; pmr (deuteriochloroform):  $\delta$  1.17 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>C), 2.02 (s, 3H, CH<sub>3</sub>), 6.1 (m, 2H, H-7 and H-9), 7.27 [t (J = 8 Hz), 1H, H-8].

Anal. Calcd. for C<sub>13</sub>H<sub>13</sub>N<sub>5</sub>; C, 64.70; H, 6.27; N, 29.02. Found: C, 64.82; H, 6.55; N, 28.82.

2-*t*-Butyl-5-(2-phenylethenyl)-1,3,4,6,9b-pentaazaphenalene (**6**).

A mixture of 2.41 g. (0.01 mole) of **2**, 1.59 g. (0.015 mole) of benzaldehyde and 10 ml. of acetic anhydride was stirred and refluxed for 17 hours. Upon cooling to room temperature, 1.43 g., m.p. 251-254° (44%) of **6** crystallized and was collected by filtration and washed with ether. Recrystallization from toluene gave purple crystals, m.p. 254-256°; pmr (deuteriochloroform):  $\delta$  1.20 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>C), 5.99 [d (J = 8 Hz), 2H, H-7 and H-9], 6.4 [d (J = 16 Hz), 1H, C=CH], 6.98-7.5 (m, 6H, phenyl-H and H-8), 7.8 [d (J = 16 Hz), 1H, C=CH].

Anal. Calcd. for C<sub>20</sub>H<sub>19</sub>N<sub>5</sub>; C, 72.92; H, 5.81; N, 21.26. Found: C, 72.83; H, 5.71; N, 21.31.

2-*t*-Butyl-5-(2-*p*-nitrophenylethenyl)-1,3,4,6,9b-pentaazaphenalene (**7**).

The procedure used to prepare **6** was followed exactly except that 1.81 g. (0.012 mole) of *p*-nitrobenzaldehyde was used in place of benzaldehyde together with 15 ml. of acetic anhydride. There was obtained 1.87 g. (50%) of crude **7**, m.p. 290-293°. Recrystallization from toluene gave green crystals, m.p. 293-294°; pmr (deuteriochloroform):  $\delta$  1.14 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>C), 6.07 [d (J = 8 Hz) 2H, H-7 and H-9], 6.52 [d (J = 16 Hz), 1H, C=CH], 7.02-7.51 (m, 3H, H-8 and phenyl H-2 and H-6), 7.74 [d (J = 16 Hz), 1H, C=CH], 8.17 [d (J ~ 8 Hz), 2H, phenyl H-3 and H-5].

Anal. Calcd. for C<sub>26</sub>H<sub>18</sub>N<sub>5</sub>O<sub>2</sub>; C, 64.16; H, 4.85; N, 22.45. Found: C,

63.95; H, 4.70; N, 22.57.

2-*t*-Butyl-5-(2-*p*-tolylethenyl)-1,3,4,6,9b-pentaazaphenalene (**8**).

The procedure used to prepare **6** was followed exactly except that 1.19 g. (0.0099 mole) of *p*-tolualdehyde was used in place of benzaldehyde. The crude product obtained was chromatographed on 60 g. of silica using methylene chloride/ethyl acetate (95/5) as eluent. The purple fraction yielded 0.30 g. (8.7%) of **8**, m.p. 318-319°. Recrystallization from toluene gave purple needles with no change in melting point; pmr (deuteriochloroform):  $\delta$  1.18 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>C), 2.35 (s, 3H, CH<sub>3</sub>), 6.08 [d (J = 8 Hz), 2H, H-7 and H-9], 6.58 [d (J = 16 Hz), 1H, C=CH], 7.03-7.6 (m, 5H, phenyl-H and H-8), 7.88 [d (J = 16 Hz), 1H, C=CH].

*Anal.* Calcd. for C<sub>21</sub>H<sub>21</sub>N<sub>5</sub>: C, 73.44; H, 6.16; N, 20.40. Found: C, 73.56; H, 6.05; N, 20.57.

1,4-Bis[2-(2-*t*-butyl-1,3,4,6,9b-pentaazaphenalene-5-yl)ethenyl]benzene (**9**).

A mixture of 5.3 g. (0.022 mole) of **2**, 1.34 g. (0.01 mole) of terephthal-dicarboxaldehyde and 20 ml. of acetic anhydride was refluxed for 17 hours. The heavy precipitate that formed was collected by filtration and washed with ether, 2.65 g. (46%), m.p. 370-378° dec. Very low solubility precluded recrystallization but an analytical sample was obtained by boiling a small portion of **9** in DMF. The insoluble metallic green crystals obtained by hot filtration melted 382-384° dec.; ir (Nujol):  $\lambda$  5.70-6.0 transparent, 6.09 (C=C).

*Anal.* Calcd. for C<sub>34</sub>H<sub>32</sub>N<sub>10</sub>: C, 70.32; H, 5.56; N, 24.10. Found: C, 70.13; H, 5.51; N, 23.91.

2-*t*-Butyl-5-ethyl-1,3,4,6,9b-pentaazaphenalene (**10**).

The preparation of **10** illustrates the method used to prepare the other alkylated derivatives of **2** shown below.

A stirred solution (26°) of 2.41 g. (0.01 mole) of **2** in 40 ml. of dry DMF (nitrogen atmosphere) was treated with 0.48 g. (0.01 mole, 50% oil dispersion) of sodium hydride. The mixture was allowed to stir one half hour at ambient temperatures, then heated to 40°, after which it was allowed to cool to room temperature over 1 hour. Chilling of the dark red solution to 15° was followed by the addition of 14.2 g. (0.1 mole) of methyl iodide in one portion. A slight exotherm was noticed and the mixture was stirred for an additional hour. The residue obtained after removal of the DMF and excess methyl iodide, first at the water aspirator and then under a pressure ~ 4 mm., was taken up in 100 ml. of chloroform, filtered through a mat of Celite (filter aid) and the filtrate was evaporated to dryness. This residue (referred to as residue "A" in the other alkylation reactions shown below) was dissolved in 5 ml. of chloroform and chromatographed on 30 g. of silica using methylene chloride/ethyl acetate (90/10) as eluent. Evaporation of the first fraction (red) off the column gave 0.22 g. (9%) of **10**, m.p. 193-195°. Later fractions proved to be unresolved mixtures (tlc) of what appeared to be more highly alkylated products (nmr analysis); a considerable tarry layer was retained by the column. Recrystallization of crude **10** from petroleum ether (110-120°) gave red plates, m.p. 195-196°; pmr (deuteriochloroform):  $\delta$  0.98-1.38 [t and s overlapping, 12H, CH<sub>3</sub> and (CH<sub>3</sub>)<sub>3</sub>C], 2.31 [q (J = 7 Hz), 2H, CH<sub>2</sub>], 6.14 (m, 2H, H-7 and H-9), 7.28 [t (J = 8 Hz), 1H, H-8].

*Anal.* Calcd. for C<sub>14</sub>H<sub>17</sub>N<sub>5</sub>: C, 65.86; H, 6.71; N, 27.43. Found: C, 65.50; H, 6.67; N, 27.61.

Use of lesser amounts of methyl iodide in the above reaction gave lower amounts of **10**.

2-Butyl-5-*t*-butyl-1,3,4,6,9b-pentaazaphenalene (**11**).

The procedure used to prepare compound **10** was followed exactly except an equivalent molar portion of propyl bromide was used in place of methyl iodide.

Residue "A" was dissolved in 5 ml. of chloroform and chromatographed on 30 g. of silica using methylene chloride/ethyl acetate (95/5) as eluent. Evaporation of the first fraction (red) off the column gave 0.34 g. (12%) of **11**, m.p. 143-145°; the next fraction (red) afforded a gummy solid that resisted further purification, but appeared to be largely the

dialkylated product (nmr analysis). Recrystallization of crude **11** from petroleum ether (110-120°) gave a fluffy pink solid, m.p. 147-148°; pmr (deuteriochloroform):  $\delta$  0.9-1.7 [m (broad) and s overlapping, 16H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub> and (CH<sub>3</sub>)<sub>3</sub>C], 2.20 [t (broad, J ~ 7 Hz), 2H, CH<sub>2</sub>], 6.10 (m, 2H, H-7 and H-9), 7.25 [t (J = 8 Hz), 1H, H-8].

*Anal.* Calcd. for C<sub>16</sub>H<sub>21</sub>N<sub>5</sub>: C, 67.81; H, 7.47; N, 24.72. Found: C, 67.69; H, 7.56; N, 24.54.

2-*t*-Butyl-5-heptyl-1,3,4,6,9b-pentaazaphenalene (**12**).

The procedure used to prepare compound **10** was followed exactly except an equivalent molar portion of hexyl bromide was used in place of methyl iodide.

Residue "A" was dissolved in 5 ml. of chloroform and chromatographed on 50 g. of silica using methylene chloride/ethyl acetate: 95/5 as eluent. The first fraction (red) off the column gave upon evaporation 0.26 g. (8%) of **12**, m.p. 90-92°. Recrystallization from petroleum ether (60-75°) gave a pink granular solid, m.p. 99-100°; pmr (deuteriochloroform):  $\delta$  0.87-1.65 [m (broad) and s overlapping, 22H, CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub> and (CH<sub>3</sub>)<sub>3</sub>C], 2.19 [t (broad, J ~ 7 Hz), 2H, CH<sub>2</sub>], 6.07 (m, 2H, H-7 and H-9), 7.27 [t (J = 8 Hz), 1H, H-8].

*Anal.* Calcd. for C<sub>19</sub>H<sub>27</sub>N<sub>5</sub>: C, 70.12; H, 8.36; N, 21.52. Found: C, 69.84; H, 8.44; N, 21.57.

2-( $\alpha,\alpha$ -Dibenzylmethyl)-5-*t*-butyl-1,3,4,6,9b-pentaazaphenalene (**13**).

The procedure used to prepare compound **10** was followed exactly except an equivalent molar portion of benzyl chloride was used in place of methyl iodide.

Residue "A" was dissolved in 5 ml. of chloroform and chromatographed on 60 g. of silica gel using methylene chloride/ethyl acetate (95/5) as eluent. Evaporation of the first fraction (red) off the column gave 0.44 g. (10%) of **13**, m.p. 177-179°. The second fraction (red) gave a small amount (0.03 g.) of what appeared to be largely monoalkylated product (nmr analysis); efforts to obtain a sample suitable for analysis from this material or to improve its yields by varying the reaction conditions failed. Recrystallization of crude **13** from toluene/petroleum ether (110-120°) gave red crystals, m.p. 185-186°; pmr (deuteriochloroform):  $\delta$  1.18 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>C), 2.5-3.0 [m (broad), 5H, (CH<sub>2</sub>)<sub>2</sub>CH], 5.93 (m, 2H, H-7 and H-9), 7.15 (m, 11H, phenyl-H and H-8).

*Anal.* Calcd. for C<sub>27</sub>H<sub>27</sub>N<sub>5</sub>: C, 76.93; H, 6.46; N, 16.62. Found: C, 77.12; H, 6.31; N, 16.66.

2-Formyloxy-5-methyl-1,3,4,6,9b-pentaazaphenalene (**14**).

A stirred mixture of 6.12 g. (0.022 mole) of **3**, 2.99 g. (0.044 mole) of dry sodium formate, 5.82 g. (0.022 mole) of 18-crown-6 and 105 ml. of dry acetonitrile was refluxed for 24 hours. The reaction mixture was evaporated to dryness and the residue after being taken up in 175 ml. of chloroform was washed with 100 ml. of water. The aqueous layer was washed with 2 x 50 ml. portions of chloroform and the combined chloroform extracts were dried (sodium sulfate) and evaporated to dryness. The tacky residue was boiled with 30 ml. of chlorobenzene, filtered and the filtrate on cooling to room temperature was treated with 30 ml. of petroleum ether (60-75°). The precipitate which formed, was collected by filtration, 2.0 g. (37%) of a reddish-purple solid, m.p. 200-203°. Recrystallization from toluene gave purple plates, m.p. 205-207°; ir (Nujol):  $\lambda$   $\mu$ m 5.83 (C=O); pmr (DMSO-*d*<sub>6</sub>):  $\delta$  1.87 (s, 3H, CH<sub>3</sub>), 4.61 (s, 2H, CH<sub>2</sub>O), 6.21 [d (J ~ 8 Hz), 2H, H-7 and H-9], 7.62 [t (J ~ 8 Hz), 1H, H-8], 8.49 (s, 1H, HCOO).

*Anal.* Calcd. for C<sub>11</sub>H<sub>9</sub>N<sub>5</sub>O<sub>2</sub>: C, 54.32; H, 3.73; N, 28.79. Found: C, 54.50; H, 4.10; N, 28.53.

2-Acetyloxymethyl-5-methyl-1,3,4,6,9b-pentaazaphenalene (**15**).

A stirred mixture of 1.0 g. (0.0036 mole) of **3**, 0.707 g. (0.0072 mole) of 18-crown-6, and 20 ml. of dry acetonitrile was refluxed for 75 minutes. The reaction mixture was evaporated to dryness and the residue after being taken up in 50 ml. of chloroform was washed with 2 x 25 ml. portions of water, dried (sodium sulfate) and evaporated to dryness. The residue on trituration with petroleum ether (60-75°) gave 0.47 g. (51%) of pink

crystals which on collection by filtration and air drying melted 172-182°. Two recrystallizations from carbon tetrachloride gave the analytical sample, pink crystals, m.p. 189-191°; ir (Nujol):  $\lambda$   $\mu$ m 5.73 (C=O); pmr (deuteriochloroform):  $\delta$  2.00 (s, 3H, CH<sub>3</sub>C=O), 2.10 (s, 3H, CH<sub>3</sub>), 4.50 (s, 2H, CH<sub>2</sub>O), 6.11 [d (J = 8 Hz), 2H, H-7 and H-9], 7.30 [t (J = 8 Hz), 1H, H-8].

*Anal.* Calcd. for C<sub>12</sub>H<sub>11</sub>N<sub>5</sub>O<sub>2</sub>: C, 56.02; H, 4.31; N, 27.23. Found: C, 55.82; H, 4.43; N, 26.99.

#### 2-Benzoyloxymethyl-5-methyl-1,3,4,6,9b-pentaazaphenalene (16).

A stirred mixture of 1.0 g. (0.0036 mole) of **3**, 1.15 g. (0.0072 mole) of anhydrous potassium benzoate, 1.0 g. (0.0036 mole) of 18-crown-6 and 20 ml. of dry acetonitrile was refluxed for 24 hours. The reaction mixture was evaporated to dryness and the residue after being taken up in 60 ml. of chloroform, was washed with 25 ml. of water, dried (sodium sulfate) and evaporated to dryness. The tacky residue resisted efforts to induce it to crystallize and so was dissolved in 10 ml. of a solution of chloroform/ethyl acetate/methanol (90/10/2), and was chromatographed over 30 g. of silica gel using the same solvent mixture for elution. Concentration of the first band (red) off the column gave 0.21 g. (18%) of **16**, m.p. 211-215°. Recrystallization from toluene gave red crystals, m.p. 218-219°; ir (Nujol):  $\lambda$   $\mu$ m 5.83 (C=O); pmr (low solubility precluded pmr analysis).

*Anal.* Calcd. for C<sub>17</sub>H<sub>13</sub>N<sub>5</sub>O<sub>2</sub>: C, 63.94; H, 4.10; N, 21.93. Found: C, 63.77; H, 4.12; N, 21.69.

#### 2-Hydroxymethyl-5-methyl-1,3,4,6,9b-pentaazaphenalene (17).

A solution of 1.21 g. (.005 mole) of **14**, 0.42 g. (0.006 mole) of pyrrolidine and 20 ml. of chloroform was stirred for 24 hours at room

temperature, filtered to remove a trace of insolubles, concentrated to 10 ml. and chromatographed over 60 g. of silica gel using chloroform/methanol/pyrrolidine (95/5/0.5) as eluent. The first fraction (red) coming off the column proved to be crude starting material (0.05 g.); evaporation of the second fraction (red) gave 0.2 g. (19%) of crude **17**, m.p. 340°. Recrystallization from chlorobenzene/petroleum ether (60-75°) gave a dull red solid, m.p. 340°; ir (Nujol):  $\lambda$   $\mu$ m 3.05 (broad, OH), 5.6 (no significant absorption); pmr (acetic acid-d<sub>4</sub>):  $\delta$  2.16 (s, 3H, CH<sub>3</sub>), 4.18 (s, 2H, CH<sub>2</sub>O), 6.48 (m, 2H, H-7 and H-9), 7.58 [t (J ~ 8 Hz), 1H, H-8].

*Anal.* Calcd. for C<sub>10</sub>H<sub>9</sub>N<sub>5</sub>O: C, 55.80; H, 4.21; N, 32.54. Found: C, 55.94; H, 4.07; N, 32.55.

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