Fused *s*-Triazino Heterocycles. IV. Electrophilic Aromatic Substitution Reactions of Some 1,3,4,6,9b-Pentaazaphenalenes (1)

John T. Shaw, C. Maury Balik (2), J. Larry Holodnak (2), and Suzanne Prem (2)

Department of Chemistry, Grove City College, Grove City, Pennsylvania 16127

Received September 8, 1975

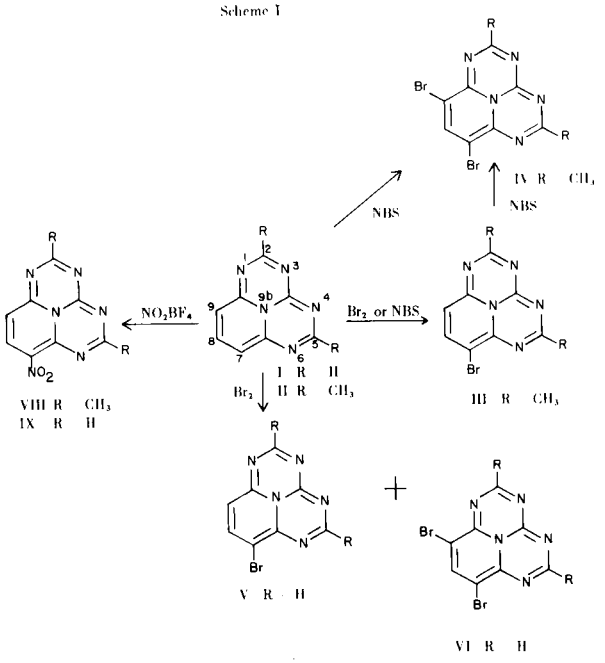
A new ring system, 1,3,4,6,9b-pentaazaphenalene (I), and various 2,5-disubstituted derivatives were reported in a previous publication (1a). The present paper describes the results of some typical electrophilic aromatic substitution reactions on this ring system, using I and 2,5-dimethyl-1,3,4,6,9b-pentaazaphenalene (II) as substrates in most of the reactions.

Room temperature bromination of II using bromine (equimolar) in methylene chloride or *N*-bromosuccinimide (NBS) (equimolar) in refluxing chloroform, gave 7-bromo-2,5-dimethyl-1,3,4,6,9b-pentaazaphenalene (III) in 69 and 79% yields (3), respectively. There was no evidence of any dibromo formation. Assignment of the bromine to position-7 in III follows nicely from the pmr spectra: a sharp 6-proton singlet found at δ 2.02 (2 CH_3) in II (1a) was now split into two sharp 3-proton singlets δ 2.06 (CH_3) and δ 2.13 (CH_3) due to lack of symmetry in III; the 2-proton doublet at δ 6.10 found in II for H_7 and H_9 was now a 1-proton doublet at δ 6.0 (J = 8 Hz), H_9, (coupling with H_8); the 1-proton triplet found at δ 7.28 in II for H_8 is now a 1-proton doublet at δ 7.53 (J = 8 Hz), H_8, (coupling with H_9). Use of peroxides and light in the NBS bromination gave III only and in essentially the same yield (81%). Dibromination of II to give 7,9-dibromo-2,5-dimethyl-1,3,4,6,9b-pentaazaphenalene (IV) (43% yield) was effected using excess NBS (3/1) in refluxing chloroform; IV was also obtained (64% yield) from III using a slight excess of NBS (1.25/1). Pmr supports the symmetrical assignment of bromine to positions 7 and 9 in IV: a 6-proton singlet at δ 2.13 (2 CH_3) and a 1-proton singlet at δ 7.80, H_8. Bromination of I using bromine in methylene chloride-tetrachloroethane at room temperature gave both 7-bromo-1,3,4,6,9b-pentaazaphenalene (V) and 7,9-dibromo-1,3,4,6,9b-pentaazaphenalene VI in 9 and 22% yields, respectively. Pmr gave data supporting assignments in V and VI: thus the 2-proton doublet found at δ 6.09 in I (H_7 and H_9) (1a), now in V was a 1-proton doublet, δ 6.08 (J = 8 Hz) H_9 (ortho coupling with H_8); the 2-proton singlet at δ 7.29 for H_2 and H_5 in I was split in the unsymmetrical V into two 1-proton singlets at δ 7.30 and 7.39, H_2 or H_5; the 1-proton triplet at δ 7.26 (H_8) in I was now a 1-proton doublet (ortho coupling with H_9) at δ 7.56 (J = 8 Hz) in V; the symmetry of VI was reflected by a 2-proton singlet at δ 7.50 (H_2 and H_5) and a 1-proton singlet at δ 8.2 (H_8). The reaction of NBS and I led to complex mixtures containing V, VI and several other contaminants whose presence were never completely eliminated.

One of the possible and indeed, desired products in the NBS bromination of II was 2-bromomethyl-5-methyl-1,3,4,6,9b-pentaazaphenalene (VII), a compound potentially quite useful in displacement reactions. Since none of VII appeared forthcoming from the current reaction series, we prepared VII using a method (1a) reported recently for the preparation of unsymmetrical 1,3,4,6,9b-pentaazaphenalenes. Thus, reaction of bromoacetyl bromide with *N*-cyano-*N'*-(6-amino-2-pyridyl)acetamidine in the presence of pyridine gave VII in 66% yield.

Nitration of the pentaazaphenalene system proved to be more difficult than bromination. Cupric nitrate-acetic anhydride mixtures which were useful in nitrating cycl-[3.2.2]azine (4) failed in this series as did tetranitromethane, and sulfuric acid-nitric acid mixtures. Low

Scheme I

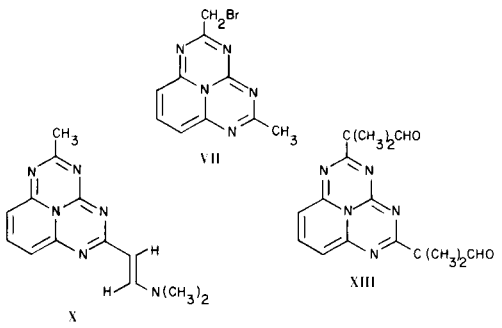


yields of 2,5-dimethyl-7-nitro-1,3,4,6,9b-pentaazaphenalene (VIII) and 7-nitro-1,3,4,6,9b-pentaazaphenalene (IX), 16 and 7% yields respectively, were obtained using nitronium tetrafluoroborate (equimolar). Pmr data for VIII and IX were quite similar in pattern to the corresponding monobromo-derivatives III and V (except that in VIII the methyl signal is a 6-proton singlet) and support the assignment of the nitro groups to position 7 in each case. Attempts to dinitrate II using excess nitronium tetrafluoroborate were unsuccessful as was the effort to convert VIII to a dinitro derivative.

Friedel-Crafts acylation of I or II using acetyl chloride or benzoyl chloride with aluminum chloride or stannic chloride gave no reaction; a similar result occurred using mixtures of trifluoroacetic anhydride with acetic acid or benzoic acid. Vilsmeier formylation of II using phosphorus oxychloride-dimethyl formamide gave 2-methyl-5-(2-dimethylaminoethenyl)-1,3,4,6,9b-pentaazaphenalene (X) in 25% yield rather than an aldehyde derivative. Meerwein, *et al.*, (5) showed that similar condensations with active methylene compounds could be achieved with dimethyl formamide dialkyl acetals. A reaction of II with dimethyl formamide diethyl acetal (equimolar) gave (X) in 88% yield; excess acetal (2/1) gave only (X), in about the same yield. No reaction occurred with I under either of these conditons. While X could exist as *cis-trans* isomers, only one compound was isolated; coupling constants for the ethylenic hydrogens (J = 12 Hz) do not allow a strong preference, but steric considerations would suggest we have a *trans* isomer. A few piloting experiments showed that similar condensations of II take place with aromatic aldehydes; these will be reported in a future paper.

Since II showed some susceptibility to the Vilsmeier reagent; it was of interest to try a substituted derivative of I in which condensation of the type exhibited by II would be prevented. A small sample of 2,5-diisopropyl-1,3,4,6,9b-pentaazaphenalene (XI) was prepared from 2,6-diaminopyridine and methyl *N*-cyanoisobutyrimidate (XII) following a procedure developed earlier (1a); the low yield obtained in this reaction (6%) discouraged us from attempting the corresponding di-*t*-butyl derivative. Reaction of XI with excess Vilsmeier reagent did give rise to an aldehyde but not the desired one. Most surprisingly, 2,5-*bis*(2,2-dimethylacetaldehyde) 1,3,4,6,9b-pentaazaphenalene (XIII) was formed in 7% yield rather than a ring-substituted carbaldehyde. Support for the proposed structure of XIII was afforded by elemental analysis, absorption in the carbonyl region of the infrared, and the pmr data: a 12-proton singlet (4 CH_3); the typical doublet-triplet absorption for H_7, H_8 and H_9 and a 2-proton singlet at δ 9.59 (2 HC=O).

Figure 1



Reactions of these new compounds will be the subject of a future paper.

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 Infracord, Model 137. Pmr spectra were determined on a Varian EM-360 spectrometer using TMS as an internal reference. Analyses were performed by Micro-Analysis Inc., Marshallton, Delaware.

Dimethylformamide, 1,2-dimethoxyethane, 1,1,2,2-tetrachloroethane and chloroform were dried using standard methods and stored over molecular sieves. *N*-Bromosuccinimide, nitronium tetrafluoroborate[0.5 *M* in sulfolane (tetramethylene sulfone)], dimethylformamide diethyl acetal, and bromoacetyl bromide, were obtained from Aldrich Chemical Company. Woelm silica gel (70-230 mesh) for column chromatography was obtained from ICN Pharmaceutical, Inc. Tlc was performed on alumina and silica gel Chromagram sheets supplied by Eastman Kodak Company. 1,3,4,6,9b-Pentaazaphenalene (I) and 2,5-dimethyl-1,3,4,6,9b-pentaazaphenalene (II) were prepared by methods given in the literature (1a).

Some of the low yields obtained from the reactions of I and II with electrophilic reagents were probably in part due to the hydrolytic conditions encountered in the work-up of some of the products. To illustrate, we found that after stirring 0.5 g. of II with 5 ml. of 0.1 *N* and 1.0 *N* hydrochloric acid for one half hour, only 50 and 0%, respectively, were recovered; using 5 ml. of 0.1 *N* and 1.0 *N* sodium hydroxide and the same conditions returned 82 and 38% of II.

7-Bromo-2-,5-dimethyl-1,3,4,6,9b-pentaazaphenalene (III).

A. Using Bromine.

A stirred solution of 1.99 g. (0.01 mole) of II in 160 ml. of methylene chloride was treated in one portion with 50 ml. of a 0.2 molar solution of bromine in methylene chloride (0.01 mole) and a precipitate formed immediately. The mixture was stirred for one hour at room temperature and filtered, orange crystals, 3.12 g., m.p. >360°; the filtrate, "A" was kept and yielded a small amount of additional III as shown below. The crude hydrobromide salt was stirred with 200 ml. of chloroform and neutralized with portions of 5% sodium bicarbonate to ~*p*H 8. The chloroform layer was separated, washed with water, dried and concentrated *in vacuo* to give 1.8 g. of crude III; m.p. indeterminate; tlc (alumina/chloroform) showed starting material as the only contaminant. Recrystallization from 2-methoxyethanol gave an

analytical sample, purple crystals, m.p. 281-283° dec.

Anal. Calcd. for $C_{10}H_8BrN_5$: C, 43.18; H, 2.90; N, 25.18. Found: C, 42.92; H, 3.02; N, 24.96.

Filtrate "A" was concentrated *in vacuo* to 10 ml. and chromatographed over 30 g. of neutral alumina (chloroform/ethyl acetate: 80/20) to give an additional 0.11 g. of crude III as the only useful fraction; combined yield of III, 1.91 g. 69%. Use of bromine in acetic acid as the brominating agent resulted in a 45 and 5% yield of III and IV, respectively.

B. Using *N*-bromosuccinimide.

A mixture of 1.0 g. (0.005 mole) of II, 0.89 g. (0.005 mole) of *N*-bromosuccinimide, and 45 ml. of chloroform was refluxed for 1.5 hours in a moisture-free atmosphere. The insoluble material was removed by filtration and the filtrate was concentrated *in vacuo* to give 1.72 g. of solid. A slurry of 10 ml. of water and this solid was stirred for 15 minutes, filtered and dried; 1.1 g. (79%, m.p. 274-276° dec., recrystallization from 2-methoxyethanol gave purple crystals identical to III prepared as in part "A". The above reaction was repeated with the addition of 0.1 g. benzoyl peroxide and the use of a 275 watt sun lamp as a source of heat and light. The results were essentially the same, 81% crude yield of III.

7,9-Dibromo-2,5-dimethyl-1,3,4,6,9b-pentaazaphenalene (IV).

A. From II and *N*-bromosuccinimide (NBS).

A mixture of 1.99 g. (0.01 mole) of II, 5.34 g. (0.03 mole) of NBS and 120 ml. of chloroform was refluxed for 72 hours and then filtered at room temperature. Concentration of the filtrate *in vacuo*, followed by stirring of the residue with 30 ml. of water gave 3.4 g. of a purple solid, m.p. indeterminate. A 1 g. portion of this solid was dissolved in 20 ml. of chloroform and chromatographed on 50 g. of silica gel using chloroform/ethyl acetate: 90/10 as the eluent. The first fractions coming off the column proved to be a mixture of II and III (recrystallization from 2-methoxyethanol gave 0.1 g. of III); IV came off as a final purple band, 0.45 g. (43% based on 3.4 g. of crude), m.p. 245-248° dec. Recrystallization from chloroform-petroleum ether (60-75°) gave an analytical sample of IV (purple crystals), m.p. 250-252° dec.

Anal. Calcd. for $C_{10}H_7Br_2N_5$: C, 33.64; H, 1.98; N, 19.62. Found: C, 33.71; H, 1.80; N, 19.56.

B. From III and NBS.

A mixture of 1 g. (0.0036 mole) of III, 0.8 g. (0.0045 mole) of *N*-bromosuccinimide and 50 ml. of chloroform was refluxed for 48 hours and then concentrated to dryness *in vacuo*. The residue was stirred with 5 ml. of water for 15 minutes, dried, and chromatographed on 50 g. of silica gel as in part "A": 0.82 g. of crude IV, (64%), m.p. 240-248° was obtained. Recrystallization as in part "A" gave IV identical to that prepared in part "A".

7-Bromo-1,3,4,6,9b-pentaazaphenalene (V) and 7,9-Dibromo-1,3,-4,6,9b-pentaazapehenalene (VI).

A stirred solution of 2.14 g. (0.0125 mole) of I in 150 ml. of dry 1,1,2,2,-tetrachloroethane was treated in one portion with 67 ml. of a 0.187 molar solution of bromine in methylene chloride (0.0125 mole) and a precipitate formed immediately. The mixture was stirred at room temperature for one hour and filtered, orange crystals, 3.17 g., m.p. 360°; the filtrate "A" was set aside and worked up as given below. The crude hydrobromide salt was stirred with 200 ml. of chloroform and neutralized with a slight excess of triethylamine; completeness of neutralization was indicated by disappearance of the orange salt and a *p*H ~ 8-9. Concentration of the mixture *in vacuo* yielded a mushy residue which crystallized on the addition of ~40 ml. of ether. The solid was collected by filtration and dried, 3.76 g. A 1.88 g. portion of this material was dissolved in 15 ml. of ethyl acetate and chromatographed over 50 g. of silica gel using ethyl acetate as eluent. Concentration of the first band (blue) off the column gave 0.09 g. of VI (0.18 g. based on 3.76 g. crude), m.p. 288-290° dec. Recrystallization from 2-methoxyethanol gave an analytical sample, dark-blue crystals, m.p. 338-340° dec.

Anal. Calcd. for $C_8H_3Br_2N_5$ (VI): C, 29.21; H, 0.92; N, 21.29. Found: C, 29.42; H, 1.07; N, 21.10.

Concentration of the second band (purple) off the column gave 0.24 g. of V (0.48 g. based on 3.76 g. crude), m.p. 248-250°. Recrystallization from 1,2-dimethoxyethane-petroleum ether (60-75°) gave dark-purple crystals, m.p. 260-262°.

Anal. Calcd. for $C_8H_4BrN_5$ (V): C, 38.42; H, 1.61; N, 28.01. Found: C, 38.21; H, 1.65; N, 27.82.

Filtrate "A" was concentrated to ~ 30 ml. and chromatographed as above on 50 g. of silica gel using chloroform/ethyl acetate: 90/10 as eluent. This afforded 0.17 g. and 0.20 g. of crude VI and V, respectively; combined percent yields of VI and V are 9 and 22%, respectively.

2-Bromomethyl-5-methyl-1,3,4,6,9b-pentaazaphenalene (VII).

A stirred, chilled (5°) slurry of 4.38 g. (0.025 mole) of *N*-cyano-*N'*(6-amino-2-pyridyl) acetamidine (1a), 1.98 g. (0.025 mole) of dry pyridine and 60 ml. of dry 1,2-dimethoxyethane was treated dropwise with 12.1 g. (0.06 mole) of bromoacetyl bromide; an exothermic reaction brought the temperature to 15°. The mixture was heated to reflux and after 15 minutes of refluxing, required 20 ml. additional 1,2-dimethoxyethane to permit efficient stirring of the thick mixture. Refluxing was continued for three hours and then the cooled mixture was filtered. The orange, ether-washed hydrobromide salt was stirred with 40 ml. of cold methanol and neutralized to *p*H ~8 with 1*N* sodium methoxide. The filtrate from this mixture was evaporated to almost dryness *in vacuo* and the residue was collected with the aid of diethyl ether. Extraction of this solid with 2 x 50 ml. portions of boiling chloroform and concentration of the combined extracts *in vacuo* gave 4.62 (66%) m.p. 200-210° dec. Recrystallization from 2-methoxyethanol and then acetonitrile gave a lavender solid, m.p. 205-207° dec. (m.p. depends on rate of heating and reported m.p. was obtained by plunging a capillary into a bath at 200° and then heating fairly rapidly); pmr (deuteriochloroform): δ 2.06 (s, 3H, CH_3), 3.76 (s, 2H, CH_2Br), 6.15 [d (J = 8 Hz), 2H, H_7 and H_9], 7.30 [t (J = 8 Hz), 1H, H_8].

Anal. Calcd. for $C_{10}H_8BrN_5$: C, 43.18; H, 2.90; N, 25.18. Found: C, 42.90; H, 2.60; N, 25.17.

2-5-Dimethyl-7-nitro-1,3,4,6,9b-pentaazaphenalene (VIII).

A stirred thin slurry of 1 g. (0.005 mole) of II in 80 ml. of dry acetonitrile was treated in one portion with 10 ml. of a 0.5 molar nitronium tetrafluoroborate (in sulfolane) solution (0.005 mole) under a nitrogen atmosphere. The resulting amber solution was stirred at room temperature for one hour, and then concentrated *in vacuo* (pot temperature $<30°$) to a thin oil. This oil was taken up in 80 ml. of chloroform and washed with 2 x 20 ml. of 5% sodium bicarbonate, then 20 ml. of water, dried (sodium sulfate) and then concentrated under reduced-pressure. The residue, an amber oil, was chromatographed over 50 g. of silica gel. Elution with methylene chloride removed the sulfolane; further elution with chloroform/ethyl acetate: 90/10 carried off VIII as an orange-red band: 0.20 g. (16%) m.p. 280-285° dec. Recrystallization from 2-methoxyethanol gave bright orange crystals, m.p. 287-288° dec. (vigorous); ir λ (Nujol): 7.59 μ (NO_2); pmr (DMSO-d_6):

δ 2.06 (s, 6H, $2CH_3$), 6.13 [d (J ~10 Hz), 1H, H_9], 8.07 [d (J ~ 10 Hz), 1H, H_8].

Anal. Calcd. for $C_{10}H_8N_6O_2$: C, 49.18; H, 3.30; N, 34.42. Found: C, 49.05; H, 3.48; N, 34.21.

7-Nitro-1,3,4,6,9b-pentaazaphenalene (IX).

The reaction conditions for preparing VIII were followed except 0.86 g. (0.005 mole) of I was used and elution with methylene chloride was followed by elution with chloroform/-ethyl acetate - 80/20: 0.08 g. (7%) m.p. 270-280° dec. Recrystallization from 2-methoxyethanol gave red crystals, m.p. 303-305° dec.; ir λ (Nujol): 6.5 μ (NO_2); pmr (DMSO-d_6): δ 6.20 [d (J ~9 Hz), 1H, H_9], 7.74 (s, 1H, H_2 or H_5), 7.77 (s, 1H, H_2 or H_5), 8.08 [d (J ~9 Hz), 1H, H_8].

Anal. Calcd. for $C_8H_4N_6O_2$: C, 44.45; H, 1.86; N, 38.88. Found: C, 44.67; H, 2.03; N, 38.87.

2-Methyl-5(2-dimethylaminoethenyl)-1,3,4,6,9b-pentaazaphenalene (X).

A. Using Vilsmeier's Reagent.

A stirred sample of 2.69 g. (0.037 mole) of dry dimethylformamide was treated dropwise with 2.30 g. (0.015 mole) of phosphorus oxychloride at 10-15° under an atmosphere of nitrogen. This solution after being stirred for fifteen minutes at room temperature, was diluted with 5 ml. of dry chloroform and added in one portion to a stirred cool (15°) solution of 1.99 g. (0.01 mole) of II in 80 ml. of dry chloroform (nitrogen atmosphere). After ten more minutes of reaction at ambient temperatures, the orange slurry was added in portions to a vigorously stirred mixture of 200 ml. of 5% sodium bicarbonate and 150 ml. of chloroform. The layers were separated and the aqueous layer was extracted with 2 x 75 ml. portions of chloroform. All chloroform extracts were combined, washed with water, dried over sodium sulfate, concentrated to ~15 ml. *in vacuo*, and chromatographed over 70 g. of silica gel using methylene chloride/-1,2-dimethoxyethane/*n*-propanol: 80/20/4 as eluent. A red band came off the column first, 0.6 g. of II: m.p. 274-277°; further elution removed an amber band of crude X, 0.44 g. (25%, based on recovered starting material), m.p. 225-228°. Two recrystallizations from toluene gave red crystals, m.p. 230-232°; ir δ (Nujol): 6.15 μ (C=C); pmr (deuteriochloroform): δ 2.04 (s, 3H, CH_3), 2.92 [s (broad) 6H, $N(CH_3)_2$], 4.79 [d (J ~12 Hz) 1H, C=CH], 5.80-6.14 [m (overlapping pair of doublet of doublets) 2H, H_7 and H_9], 7.19 [t (J = 8 Hz), 1H, H_8], 7.92 [d (J = 12 Hz) 1H, C=CH]. The analytical sample was dried for three hours over phosphorus pentoxide *in vacuo*, (toluene used in boiler).

Anal. Calcd. for $C_{13}H_{14}N_6$: C, 61.40; H, 5.55; N, 33.05. Found: C, 61.59; H, 5.76; N, 32.79.

B. Using Dimethylformamide Diethyl Acetal.

A stirred solution of 1.0 g. (0.005 mole) of II, 0.74 g. (0.005 mole) of dimethylformamide diethyl acetal and 20 ml. of dry chloroform was refluxed for 20 hours in an atmosphere protected from moisture, concentrated *in vacuo* to ~15 ml., and chromatographed over 60 g. of silica gel as in case "A" above: 0.45 g. of crude starting material, m.p. 269-273° and 0.62 g. (88%, based on recovered starting material) of crude X, m.p. 224-228° were obtained. Recrystallization from toluene gave material identical to X prepared as in case "A". Using twice the amount of *N,N*-dimethylformamide diethyl acetal gave only X and in about the same yield.

Methyl *N*-Cyanoisobutyrimidate (XII).

Using Huffman and Schaefer's method (6) a 54% crude yield of XII was obtained from methyl isobutyrimidate hydrochloride (7), and cyanamide; a second distillation at reduced pressure gave an analytical sample, b.p. 96-98° (14 mm.), m.p. 34-36°; ir λ (Nujol): 4.49 μ (C≡N).

Anal. Calcd. for $C_6H_{10}N_2O$: C, 57.12; H, 7.99; N, 22.20. Found: C, 57.37; H, 8.00; N, 22.40.

2,5-Diisopropyl-1,3,4,6,9b-pentaazaphenalene (XI).

A stirred mixture of 11.7 g. (0.107 mole) of 2,6-diaminopyridine, 32.5 g. (0.26 mole) of XII and 27 ml. of dry 1,2-dimethoxyethane was refluxed for twenty hours, then concentrated *in vacuo* to a red oil weighing 44 g. An 11 g. sample of this oil was chromatographed over 70 g. of silica gel using chloroform/ethyl acetate: 90/10 as eluent: 0.41 g. of crude XI (6% based on 44 g.) m.p. 174-178°; came off the column first (red band). Recrystallization from cyclohexane gave bright pink crystals, m.p. 178-180° (a final washing of the filter cake with a small amount of cold ether proved to be very effective in removing a troublesome contaminant); pmr (deuteriochloroform): δ 1.13 [d (J ~7 Hz), 12H, $2(CH_3)_2CH$], 2.43 [m (J ~ 7 Hz) 2H, $2(CH_3)_2CH$] 6.07 [d (J = 8 Hz), 2H, H_7 and H_9], 7.23 [t (J = 8 Hz) 1H, H_8].

Anal. Calcd. for $C_{14}H_{17}N_5$: C, 65.85; H, 6.71; N, 27.43. Found: C, 66.04; H, 6.43; N, 27.48.

2,5-*Bis*(2,2-dimethylacetaldehyde)-1,3,4,6,9b-pentaazaphenalene (XIII).

A stirred sample of 3.29 g. (0.045 mole) of dry dimethylformamide was treated dropwise with 0.74 g. (0.0048 mole) of phosphorus oxychloride at 5-12° under an atmosphere of nitrogen. The solution was then stirred at room temperature for fifteen minutes, cooled to 15° and treated in one portion with 0.41 g. (0.0016 mole) of XI dissolved in 10 ml. of dry chloroform. Continued reaction at ambient temperatures for twenty minutes was followed by a fifteen minute reflux. The cooled product (room temperature) was then added in portions to a vigorously stirred mixture of 100 ml. of chloroform and 100 ml. of 5% sodium bicarbonate. Upon completion of neutralization (final *p*H ~ 7.5), the mixture was gently boiled for fifteen minutes, cooled, and the chloroform layer was dried over sodium sulfate. Concentration of the chloroform to dryness *in vacuo* gave 0.036 g. of crude XIII, m.p. 168-172° (7%). Recrystallization from a large amount of cyclohexane gave rose crystals, m.p. 172-174°; ir λ (Nujol): 5.79 μ (C=O); pmr (deuteriochloroform): δ 1.29 (s, 12H, 2 $(CH_3)_2$ CCHO), 6.14 [d (J = 8 Hz), 2H, H_7 and H_9], 7.29 [t (J = 8 Hz), 1H, H_8], 9.62 (s, 2H, 2 CHO).

Anal. Calcd. for $C_{16}H_{17}N_5O_2$: C, 61.72; H, 5.50; N, 22.50. Found: C, 61.72; H, 5.63; N, 22.16.

When the above reaction was carried out using 0.0016 mole of phosphorus oxychloride an inseparable mixture was obtained.

Acknowledgement.

We gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society for support of this research.

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