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The trichloromethyl group served as a useful leaving group in nucleophilic displacement reactions by a variety of substituted amines and alcohols (the latter under base catalysis) on 2-trichloromethyl-5-methyl-1,3,4,6,9b-pentaazaphenalene (**1a**) and 2-trichloromethyl-4-cyano-1,3,6,9b-tetraazaphenalene (**2a**). The reaction conditions were mild and the yields of the corresponding 2-substituted amino and alkoxy derivatives were generally good.

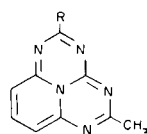
J. Heterocyclic Chem., **19**, 357 (1982).

As part of a continuing investigation of the chemistry of aza analogues of 9b-azaphenalene, the present paper reports on an attractive method for the preparation of amino and alkoxy derivatives of the 1,3,4,6,9b-pentaazaphenalene (**1**) and 1,3,6,9b-tetraazaphenalene (**2**) ring systems.

Our first efforts to achieve these ends were directed towards the preparation of 2-chloro-5-methyl-1,3,4,6,9b-pentaazaphenalene (**1t**, R = Cl). The reactive moiety of this compound bears an obvious resemblance to the halogen derivatives of *s*-triazine and we hoped it might have the enhanced reactivity toward nucleophiles that halogen derivatives of *s*-triazine (**2**) enjoy. Many attempts (involving ring closures) to prepare 2-hydroxy-5-methyl-1,3,4,6,9b-pentaazaphenalene (**1n**), a precursor we had hoped to convert to **1t**, were to no avail. Later, when **1n** became available by the nucleophilic displacement methods described below, it proved to be totally unstable to the reaction conditions normally employed for the hydroxyl to chloro group conversion (*viz.*, phosphorus oxychloride/triethylamine or thionyl chloride/DMF).

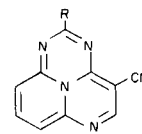
The trichloromethyl group when attached to the *s*-triazine ring system has also served as a leaving group in nucleophilic displacement reactions involving amines (**3**), and alcohols (**4**). To test the applicability of this leaving group in ring system **1**, we synthesized 2-trichloromethyl-5-methyl-1,3,4,6,9b-pentaazaphenalene (**1a**) using a general method described in an earlier paper (**5**). Thus reaction of *N*-cyano-*N'*-(6-amino-2-pyridyl)acetamide (**3**) with trichloroacetyl chloride (**4**) in the presence of pyridine gave **1a** in 48% yield. We found **1a** to react under rather mild conditions (Table 1) with ammonia, hydrazine, and various primary and secondary aliphatic amines. For example, reaction of a chloroform solution of **1a** with excess *n*-butylamine for 1 hour at room temperature gave a 48% yield of 2-*n*-butylamino-5-methyl-1,3,4,6,9b-pentaazaphenalene (**1g**). By comparison, reaction of **1a** (1 mole) with a moderately reactive nucleophilic aromatic amine, *p*-anisidine (2.4 mole), in refluxing chloroform for 48 hours gave none of the desired 2-*p*-anisidino-5-methyl-1,3,4,6,9b-pentaazaphenalene (**1j**); repeating the reaction exactly but

Figure 1



1

- 1a**, R = CCl₃
- 1b**, R = NH₂
- 1c**, R = NHNH₂
- 1d**, R = NHCH₃
- 1e**, R = NHCH₂C₆H₅
- 1f**, R = NH(CH₂)₃N(CH₃)₂
- 1g**, R = NH(CH₂)₃CH₃
- 1h**, R = NHCH(CH₃)CH₂CH₃
- 1i**, R = NH-cyclohexyl
- 1j**, R = NHC₆H₄OCH₃-*p*
- 1k**, R = N(CH₃)₂
- 1l**, R = 1-pyrrolidino
- 1m**, R = 1-piperidino
- 1n**, R = OH
- 1o**, R = OCH₃
- 1p**, R = OCH₂CH₂CH₃
- 1q**, R = OCH₂CH₂OCH₃
- 1r**, R = OCH(CH₃)₂
- 1s**, R = OCH₂CH₂N(CH₃)₂



2

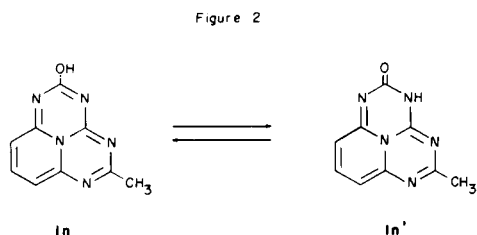
- 2a**, R = CCl₃
- 2b**, R = NH₂
- 2c**, R = NHNH₂
- 2d**, R = NH(CH₂)₃CH₃
- 2e**, R = NHCH(CH₃)CH₂CH₃
- 2f**, R = NHC₆H₄OCH₃-*p*
- 2g**, R = 1-pyrrolidino
- 2h**, R = OH
- 2i**, R = OCH₃
- 2j**, R = OCH₂CH₂CH₃
- 2k**, R = OCH₂CH₂OCH₃

including an acylation catalyst, 4-dimethylaminopyridine, (1 mole and 3 mole) gave a 13 and 68% yield, respectively, of **1j**.

Alcohols required base catalysis. Thus reaction of a refluxing methanol solution containing **1a** and a small amount of benzyltrimethylammonium methoxide for 15 minutes gave a 50% yield of 2-methoxy-5-methyl-1,3,4,6,9b-pentaazaphenalene (**1o**).

Interestingly, while suitable reaction conditions to allow displacement of the trichloromethyl group from **1a** by phenol or *p*-cresol were not found, reaction of **1a** with dilute aqueous bicarbonate to yield the 2-hydroxy derivative (**1n**) was facile, (reflux for one half hour). Solubility of **1n** in dilute sodium bicarbonate suggests a weak acid; ir and pmr spectra of **1n** support the presence of an amide group as in **1n'**. The compound probably exists as a tautomeric mixture but we will for convenience refer to **1n** as 2-hydroxy-5-methyl-1,3,4,6,9b-pentaaza-

phenalene. The anion derived from either **1n** or **1n'** would be highly resonance stabilized.

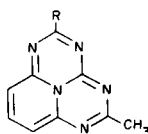


Since 2-trifluoromethyl-5-methyl-1,3,4,6,9b-pentaazaphenalene (**1u**, R = CF₃) was available from a previous investigation (5), it was of interest to compare the leaving group capability of the trifluoromethyl group versus the

trichloromethyl group. We were unable to displace the trifluoromethyl group using any of the conditions shown in Table 1, or using more vigorous conditions.

Members of both the 1,3,6,9b-tetraazaphenalene and the 1,3,5,7,9b-pentaazaphenalene ring systems have been prepared using procedures similar to that used in the preparation of **1a**. For example, reacting acetic anhydride with 2-cyano-3*N*-(6-amino-2-pyridyl)aminopropenenitrile (**5**) or 2-cyano-3*N*-(6-amino-2-pyrazinyl)aminopropenenitrile (**6**) gave 4-cyano-2-methyl-1,3,6,9b-tetraazaphenalene (**6**) and 9-cyano-2-methyl-1,3,5,7,9b-pentaazaphenalene (**7**), respectively. For purposes of studying displacement reactions on these rings by substituted-amino and alkoxy nucleophiles, we attempted to introduce the trichloromethyl group by employing trichloroacetic

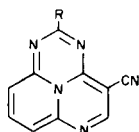
Table 1 (a)



Compound No.	R	Method	Reaction Temperature/ hours	Yield % (b)	Mp (°C) (c) Crystallization Solvent	Molecular Formula	Analysis % Calcd./Found		
							C	H	N
1b	NH ₂	A (d)	reflux/3	75	335-336 dec DMF	C ₉ H ₈ N ₆	53.99 53.63	4.03 3.98	41.98 42.03
1c	NHNH ₂	A	reflux/0.5	97	269-271 DMF	C ₉ H ₈ N ₇	50.22 49.95	4.22 4.32	45.56 45.52
1d	NHCH ₃	B	rt (e)/17	80	342-344 dec 2-methoxyethanol	C ₉ H ₁₀ N ₆	56.02 56.17	4.72 4.51	39.20 39.43
1e	NHCH ₂ C ₆ H ₅	A	reflux/24	74	257-258 chlorobenzene	C ₁₆ H ₁₄ N ₆	66.19 66.29	4.86 5.05	28.95 28.71
1f	NH(CH ₂) ₃ N(CH ₃) ₂	A (f)	reflux/2	84	218-220 benzene	C ₁₄ H ₁₉ N ₇	58.92 58.78	6.71 6.68	34.36 34.53
1h	NHCH(CH ₃)CH ₂ CH ₃	A (g)	rt/24	60	182-184 petroleum ether (100-120°)	C ₁₃ H ₁₆ N ₆	60.91 61.20	6.29 6.01	32.79 32.68
1i	NH cyclohexyl	A (h)	rt/48	59	201-203 toluene/hexane	C ₁₅ H ₁₈ N ₆	63.81 63.75	6.42 6.22	29.77 29.58
1l	1-pyrrolidino	A (h,i)	rt/1	72	230-232 toluene	C ₁₃ H ₁₄ N ₆	61.40 61.18	5.55 5.73	33.05 33.21
1m	1-piperidino	A (h)	reflux/1	75	177-178 carbon tetrachloride	C ₁₄ H ₁₆ N ₆	62.66 62.73	6.01 5.91	31.32 31.15
1p	OCH ₂ CH ₂ CH ₃	D (h)	65°/1	51	174-175 carbon tetrachloride	C ₁₂ H ₁₃ N ₅ O	59.25 59.53	5.39 5.63	28.80 29.01
1r	OCH(CH ₃) ₂	E	65°/0.5	16	191-193 toluene	C ₁₂ H ₁₃ N ₅ O	59.25 59.40	5.39 5.15	28.80 29.00
1s	OCH ₂ CH ₂ N(CH ₃) ₂	D (j)	100°/1	81	149-151 carbon tetrachloride	C ₁₃ H ₁₆ N ₆ O	57.35 57.54	5.92 6.13	30.85 30.80

(a) The ir spectra of the compounds listed support the structures shown; the pmr spectra of the compounds listed (solubility permitting) showed the expected signals for the R group and the following typical pattern: δ 6.0-6.4 (d or m) 2H, H₇ and H₉, 7.2-7.8 [t (J = 8 Hz), 1H, H₈]. (b) Crude yields, no attempt was made to optimize yields. (c) Melting point of the recrystallized product. (d) A gentle stream of ammonia was passed through the reaction mixture during the stated reaction time. (e) Room temperature. (f) 15 ml of 1,2-dimethoxyethane was used as solvent in place of chloroform. (g) Evaporated the reaction mixture to dryness and chromatographed the residue on 30 g of silica gel using ethyl acetate-methanol: 95/5. (h) Evaporated the reaction mixture to dryness and chromatographed the residue on 50 g of silica gel using methylene chloride-methanol: 95/5. (i) An amount of 0.006 mole pyrrolidine was used. (j) Addition of benzyltrimethylammonium methoxide was omitted: evaporation the reaction mixture to a thick syrup and chromatographed the residue over 30 g of neutral alumina.

Table 2 (a)



Compound No.	R	Method	Reaction Temperature/ hours	Yield % (b)	Mp (°C) (c) Crystallization Solvent	Molecular Formula	Analysis %		
							Calcd./Found	C	H
2b	NH ₂	A (d)	rt (e)/2	91	359-360 dec DMF	C ₁₀ H ₆ N ₆	57.14	2.88	39.99
							56.89	3.11	39.71
2c	NHNH ₂	A (f)	rt/24	92	318-320 dec DMF	C ₁₀ H ₇ N ₇	53.33	3.12	43.54
							53.01	3.18	43.16
2d	NH(CH ₂) ₃ CH ₃	A	rt/1	65	198-200 toluene	C ₁₄ H ₁₄ N ₆	63.14	5.29	31.56
							63.39	5.02	31.74
2e	NHCH(CH ₃)CH ₂ CH ₃	A (g)	rt/24	65	174-176 carbon tetrachloride	C ₁₄ H ₁₄ N ₆	63.14	5.29	31.56
							62.98	5.11	31.38
2f	NHC ₆ H ₄ OCH ₃ - <i>p</i>	C (h)	reflux/48	62	235-237 2-methoxyethanol	C ₁₇ H ₁₂ N ₆ O	64.55	3.83	26.57
							64.80	3.55	26.25
2g	1-pyrrolidino	A (i)	rt/20	45	274-276 toluene	C ₁₄ H ₁₂ N ₆	63.62	4.58	31.80
							63.79	4.77	32.09
2h	OH	F	reflux/0.5	87	360-362 dec DMF-ethanol	C ₁₀ H ₅ N ₅ O	56.88	2.39	33.15
							56.98	2.44	33.08
2i	OCH ₃	D (j)	reflux/1	90	245-247 dec 2-methoxyethanol	C ₁₁ H ₇ N ₅ O	58.66	3.13	31.10
							58.55	3.01	31.19
2j	OCH ₂ CH ₂ CH ₃	D (j,k)	reflux/0.5	74	174-175 toluene	C ₁₃ H ₁₁ N ₅ O	61.64	4.38	27.65
							61.73	4.49	27.75
2k	OCH ₂ CH ₂ OCH ₃	D (j,k)	reflux/0.5	70	183-185 toluene	C ₁₃ H ₁₁ N ₅ O ₂	57.99	4.12	26.00
							58.22	4.25	26.21

(a) The ir spectra of the compounds listed (with exception of **2h**, previously mentioned) support the structures shown; the pmr of the compounds listed (solubility permitting) showed the expected signals for the R group and the following typical pattern: δ 6.0-6.3 (pair of doublets or multiplet, 2H, H_i and H_j), 7.2-7.4 [t (J = 8 Hz), 1H, H_g], 7.4-7.8 (s, 1H, H_s). (b) Crude yields, no attempt was made to optimize yields. (c) Melting point of recrystallized product. (d) A gentle stream of ammonia was passed through the reaction mixture during the stated time. (e) Room temperature. (f) An amount of 0.012 mole of hydrazine hydrate was used. (g) Evaporated the reaction mixture to dryness and chromatographed the residue on 50 g of silica gel using methylene chloride-methanol: 95/5. (h) An amount of 0.005 mole of 4-dimethylaminopyridine was used. (i) An amount of 0.006 mole of pyrrolidine was used. (j) An amount of 0.0032 mole of **2a** was used. (k) A total of 9 drops of a 40% methanolic solution of benzyltrimethylammonium methoxide added in portions of 3 drops each, separated by 10 minute intervals, was used.

anhydride in place of acetic anhydride in the aforementioned procedures. Neither ring system formed; instead large amounts of tarry materials together with a heavy evolution of carbon dioxide resulted. Trichloroacetic anhydride is apparently very unstable under the reaction conditions employed. However, we were able to prepare 2-trichloromethyl-4-cyano-1,3,6,9b-tetraazaphenalene (**2a**) in 65% yield by reacting **4** with **5** under reaction conditions very similar to those used in the preparation of **1a**. The corresponding reaction of **4** with **6** gave only intractable tars.

The results of the reactions of **2a** with various amines and alcohols under reaction conditions developed for use with **1a** are shown in Table 2. Yields again were rather good. Compound **2h**, like **1n** above, probably exists as a mixture of tautomers, but is shown as a hydroxyl derivative for convenience. Its infrared spectrum in addition to possessing a cyano band at 4.55 μ m, showed absorption at 2.98 μ m (NH or OH) and 5.95 μ m (C=O); very

low solubility prevented pmr analysis.

Based on the findings of this investigation, it would appear that the trichloromethyl group provides an attractive alternative in heterocyclic displacement reactions where the leaving group normally considered would be halogen, alkylthio, or alkoxy. Work is currently underway in this laboratory to attempt the introduction of the trichloromethyl group at other positions in ring systems **1** and **2** and in other aza analogues of 9b-azaphenalene.

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-Analyses Inc., Wilmington, Delaware. All evaporations were carried out on a rotary evaporator at reduced pressure.

N,N-Dimethylformamide (DMF), 1,2-dimethoxyethane (glyme), chloroform 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: sodium hydride (50% dispersion in mineral oil), trichloroacetyl chloride, 40% benzyltrimethylammonium methoxide and 2-dimethylaminoethanol. Woelm silica gel (70-230 mesh) and neutral alumina for column chromatography were obtained from ICN Pharmaceutical Inc. *N*-cyano-*N'*-(6-amino-2-pyridyl)acetamide (**3**) (**5**), 2-cyano-3*N*-(6-amino-2-pyridyl)-aminopropenenitrile (**5**) (**6**) and 2-trifluoromethyl-5-methyl-1,3,4,6,9b-pentaazaphenalene (**1u**) (**5**) were prepared using methods described in the literature.

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

A cold (8°) stirred slurry of 13.1 g (0.075 mole) of **3**, 5.94 g (0.075 mole) of dry pyridine and 100 ml of dry glyme (nitrogen atmosphere) was treated dropwise with 32.7 g (0.18 mole) of **4** while maintaining the temperature at or slightly below 8° during the addition. The thick reaction mixture was then stirred and gently refluxed for 3 hours, cooled to room temperature, filtered and the filter cake was washed several times with ether. An ice-cold stirred slurry of the reaction product in 90 ml of methanol was carefully neutralized to ~pH 9 by the dropwise addition of 5% methanolic sodium methoxide. The purple solid obtained after filtration of the reaction mixture, washing with methanol and oven drying at 60°, was heated with 100 ml of chloroform, filtered and the filtrate was evaporated to dryness, 11.0 g (48%) mp 226-230° dec. Recrystallization from toluene gave purple crystals, mp 230-232° dec; pmr (deuteriochloroform): δ 2.10 (s, 3H, CH₃), 6.32 (m, 2H, H₇ and H₈), 7.45 [t (J = 8 Hz) 1H, H₈].

Anal. Calcd. for C₁₀H₈Cl₃N₅: C, 39.69; H, 2.00; N, 23.15. Found: C, 39.88; H, 2.06; N, 23.34.

The following examples are illustrative of the methods used to prepare the compounds listed in Tables 1 and 2. Because of poorer solubility of **2a** in chloroform, the amine reactions in Table 2 were carried out in 25 ml of chloroform rather than 15 ml.

Method A.

2-(*n*-Butylamino)-5-methyl-1,3,4,6,9b-pentaazaphenalene (**1g**).

A stirred solution of 1.5 g (0.005 mole) of **1a** and 15 ml of dry chloroform was treated at room temperature with 1.46 g (0.02 mole) of *n*-butylamine. The precipitate that had formed after stirring for 1 hour was filtered and washed with ether, 0.61 g (48%), mp 242-244°. Recrystallization from toluene did not raise the melting point; ir λ (Nujol): μ m 3.15, (NH); pmr (deuteriochloroform): δ 0.91 [t (distorted, J ~ 6 Hz), 3H, CH₃], 1.60 [m, 4H, (CH₂)₂], 2.10 (s, 3H, CH₃), 3.45 [t, (J ~ 6 Hz), 2H, CH₂], 6.11 [m, 2H, H₇ and H₈], 6.55 [s, (broad) 1H, NH], 7.35 [t (J = 8 Hz), 1H, H₈].

Anal. Calcd. for C₁₃H₁₆N₆: C, 60.92; H, 6.92; N, 32.79. Found: C, 61.22; H, 6.60; N, 33.03.

Method B.

2-Methyl-5-dimethylamino-1,3,4,6,9b-pentaazaphenalene (**1k**).

A solution of 1.14 g (0.014 mole) of dimethylamine hydrochloride and 12 ml of 1*N* sodium hydroxide was added to a stirred solution of 1.5 g (0.005 mole) of **1a** and 15 ml of dry chloroform and the mixture was stirred at room temperature for 3 days. The organic layer was separated and after extracting the aqueous layer with chloroform (3 times with 15 ml) the combined organic extracts were dried (sodium sulfate) concentrated to ~ 5 ml, and chromatographed on 25 g of silica gel using methylene chloride-methanol (95:5) as eluent. The yellow fraction was collected and yielded 0.48 g (42%) of crude **1k**, mp 199-201°. Recrystallization from toluene gave burnt-orange platelets, mp 205-207°; pmr (deuteriochloroform): δ 2.10 (s, 3H, CH₃), 3.10 [s, 6H, N(CH₃)₂], 6.03 (m, 2H, H₇ and H₈), 7.21 [t, (J = 8 Hz), 1H, H₈].

Anal. Calcd. for C₁₁H₁₂N₆: C, 57.88; H, 5.30; N, 36.82. Found: C, 58.18; H, 5.66; N, 36.58.

Method C.

2-(*p*-Anisidino)-5-methyl-1,3,4,6,9b-pentaazaphenalene (**1j**).

A stirred solution of 1.5 g (0.005 mole) of **1a**, 1.48 g (0.012 mole) of *p*-anisidine, 1.83 g (0.015 mole) of 4-dimethylaminopyridine and 15 ml of dry chloroform was refluxed for 48 hours. The insoluble material was filtered at room temperature and washed with ether, 1.04 g (68%), mp 276-278°. Recrystallization from 2-methoxyethanol gave reddish-brown crystals, mp 276-278°, ir λ (Nujol): μ m 3.10 (NH); pmr (very low solubility precluded pmr analysis).

Anal. Calcd. for C₁₆H₁₄N₆O: C, 62.73; H, 4.61; N, 27.44. Found: C, 62.51; H, 5.46; N, 27.19.

The same reaction conditions without the presence of 4-dimethylaminopyridine gave none of **1j**, use of 0.005 mole of 4-dimethylaminopyridine in above reaction gave a 13% yield of **1j**.

Method D.

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

A stirred mixture of 1.5 g (0.005 mole) of **1a** and 50 ml of methanol was heated to reflux and after refluxing for 5 minutes was treated with 7 drops of a 40% methanolic solution of benzyltrimethylammonium methoxide. Analysis (tlc) showed that after 10 minutes additional refluxing there was no longer any **1a** present. The reaction mixture which was allowed to cool to room temperature and stand overnight, deposited 0.54 g (50%) of amber crystals, mp 225-226°. Recrystallization from chlorobenzene gave golden orange crystals, mp 226-227°; pmr (DMSO-*d*₆): δ 2.01 (s, 3H, CH₃), 3.85 (s, 3H, OCH₃), 6.3 [d (J = 8 Hz), 2H, H₇ and H₈], 7.63 [t, (J = 8 Hz), 1H, H₈].

Anal. Calcd. for C₁₀H₈N₅O: C, 55.81; H, 4.22; N, 32.55. Found: C, 55.65; H, 4.27; N, 32.46.

Method E.

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

A stirred mixture of 1.5 g (0.005 mole) of **1a** and 50 ml of 2-methoxyethanol was maintained at ~ 65° while two portions, 0.06 g (0.0013 mole) each, of sodium hydride (50% oil dispersion) were added about 10 minutes apart. The amber solution was stirred an additional 20 minutes and then evaporated to dryness. The residue was taken up in 10 ml of chloroform and chromatographed over 50 g of silica gel using methylene chloride/methanol (95/5) as eluent. The orange fraction was collected and gave 0.83 g (64%) of crude **1q**, mp 145-147°. Recrystallization from carbon tetrachloride gave bright orange crystals of the same melting point; pmr (deuteriochloroform): δ 2.12 (s, 3H, CH₃), 3.4 (s, 3H, OCH₃), 3.68 [t (J = 6 Hz), 2H, CH₂], 4.45 [t (J = 6 Hz), 2H, CH₂], 6.18 [d (J ~ 8 Hz), 2H, H₇ and H₈], 7.37 [t (J ~ 8 Hz), 1H, H₈].

Anal. Calcd. for C₁₂H₁₃N₅O₂: C, 55.59; H, 5.05; N, 27.02. Found: C, 55.32; H, 4.95; N, 26.95.

Method F.

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

A vigorously stirred mixture of 1.5 g (0.005 mole) of **1a**, 1.68 g (0.02 mole) of sodium bicarbonate and 25 ml of water formed an amber solution after being refluxed for one half hour. The solution was allowed to cool to room temperature and after adjusting the pH to ~ 5.5 with 1*N* hydrochloric acid (caution, foaming), the precipitate which had formed was collected by filtration. The filter cake was washed with water and air dried to yield 0.80 g (80%) of **1n**, mp 294-296° dec. Recrystallization from ethanol gave yellow crystals, mp 323-325° dec. (Note: to obtain this melting point, a sample in a capillary tube was plunged into a melting point bath at 300° and rapidly heated to the decomposition point); ir λ (Nujol): μ m 2.92 (NH), 5.92 (C=O); pmr (DMSO-*d*₆): δ 2.2 (s, 3H, CH₃), 6.4 [d (J = 8 Hz), 2H, H₇ and H₈], 6.6 [s, 1H, NH (exchangeable with deuterium oxide)], 7.82 [t (J = 8 Hz), 1H, H₈].

Anal. Calcd. for C₉H₇N₅O: C, 53.72; H, 3.51; N, 34.81. Found: C, 53.79; H, 3.40; N, 34.80.

2-Trichloromethyl-4-cyano-1,3,6,9b-tetraazaphenalene (**2a**).

A cold (0°) stirred slurry of 15.25 g (0.082 mole) of **5**, 6.50 g (0.082 mole) of dry pyridine and 130 ml of dry glyme (nitrogen atmosphere) was

treated dropwise with 36 g (0.198 mole) of **4** while maintaining the temperature at or slightly below 5° during the addition. The mixture was allowed to warm to 15°, then gently refluxed for 3 hours, cooled to room temperature, filtered and the filter cake was washed several times with ether. A cold (-4° to 0°) stirred slurry of the reaction product in 45 ml of methanol was carefully neutralized to ~ pH 8 by the dropwise addition of 5% methanolic sodium methoxide. The purple precipitate that formed was collected by filtration, washed several times with ether, then extracted with 400 ml of boiling chloroform. Evaporation of the extracts to dryness gave a purple solid, 17.2 g (65%), mp 218-220°. Recrystallization from toluene gave purple crystals, mp 219-221°; ir λ (Nujol): μm 4.52 (CN); pmr (deuteriochloroform): δ 6.05 [d (J = 8 Hz), 1H, H₇ or H₉], 6.28 [d (J = 8 Hz), 1H, H₇ or H₉], 7.22 [t (J = 8 Hz), 1H, H₈], 7.4 (s, 1H, H₅).

Anal. Calcd. for C₁₁H₄N₅Cl₃: C, 42.26; H, 1.29; N, 22.41. Found: C, 42.57; H, 1.52; N, 22.58.

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