Fused *s*-Triazino Heterocycles. XVIII. 1,3,4,7,11c-Pentaazabenz[*de*]anthracene and 1,3,4,6,7,11c-Hexaazabenz[*de*]anthracene. Two New Ring Systems

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The reaction of 2-amino-4-chloro-6-methylpyrimidine (**3a**) with trimethylacetyl chloride gave 4-chloro-6-methyl-2-trimethylacetamidopyrimidine (**5**). This latter compound with excess anthranilonitrile gave in one step 2-*t*-butyl-5-methyl-1,3,4,7,11c-pentaazabenz[*de*]anthracene (**6a**). To prepare 2-*t*-butyl-5-dimethylamino-1,3,4,6,7,11c-hexaazabenz[*de*]anthracene (**6b**) it was found necessary to first react 2-amino-4-chloro-6-dimethylamino-*s*-triazine (**3b**) with anthranilonitrile to yield the intermediate product 2-amino-4(2-cyanoanilino)-6-dimethylamino-*s*-triazine (**4**). Reaction of the latter with trimethylacetyl chloride gave **6b**.

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Previous papers describe the preparation of substituted members of the 1,3,7,10,11c-pentaazabenz[*de*]anthracene (**2a**) [1] and 1,3,7,8,10,11c-hexaazabenz[*de*]anthracene (**2b**) [2] ring systems. In each case these ring systems were obtained from annulation reactions involving a derivative of tetraazaphenalene (**1**). The nucleophilic R-side-chain of **1** was caused to close on the neighboring nitrile group generating a derivative of **2a** or **2b**. It occurred to us that polyazabenz[*de*]anthracene ring systems might also result from the reaction of anthranilonitrile with suitably substituted pyridine, pyrimidine or *s*-triazine ring systems.

Refluxing the commercially available 2-amino-4-chloro-6-methylpyrimidine (**3a**) in toluene with trimethylacetyl chloride in the presence of 2,6-lutidine provided 4-chloro-6-methyl-2-trimethylacetamidopyrimidine (**5**) in 59% yield. This material served as a candidate with which to try the anthranilonitrile ring closure. Thus, reaction of **5** with excess anthranilonitrile in refluxing chlorobenzene provided in one step 2-*t*-butyl-5-methyl-1,3,4,7,11c-pentaazabenz[*de*]anthracene (**6a**), by way of a double ring closure. The structure of **6a** was supported by satisfactory elemental analysis, by the absence of NH, C(O), or CN absorption in the ir and the presence of appropriate pmr signals.

A similar series of steps involving an *s*-triazine derivative, 2-amino-4-chloro-6-dimethylamino-*s*-triazine (**3b**) were thwarted by the lack of reaction of the 2-amino group of **3b** with trimethylacetyl chloride. However, by rearranging the order of the reaction steps we were able to realize ring closure to a positional isomer of **2b**. Thus, reaction of **3b** with anthranilonitrile in refluxing glyme gave 2-amino-4-(2-cyanoanilino)-6-dimethylamino-*s*-triazine (**4**) in 39% yield. Conversion of **4** in one step to 2-*t*-butyl-5-dimethylamino-1,3,4,6,7,11c-hexaazabenz[*de*]anthracene (**6b**) in 32% yield was achieved by refluxing **4** with trimethylacetyl chloride in the presence of pyridine. The structure of **6b** was supported by satisfactory elemental analysis, by the absence of NH, C(O), or CN absorption in the ir and the presence of appropriate pmr signals.

We have not been able thus far to prepare any pyridine derivatives that will react with anthranilonitrile in reactions similar to those used to prepare **6a** or **6b**.

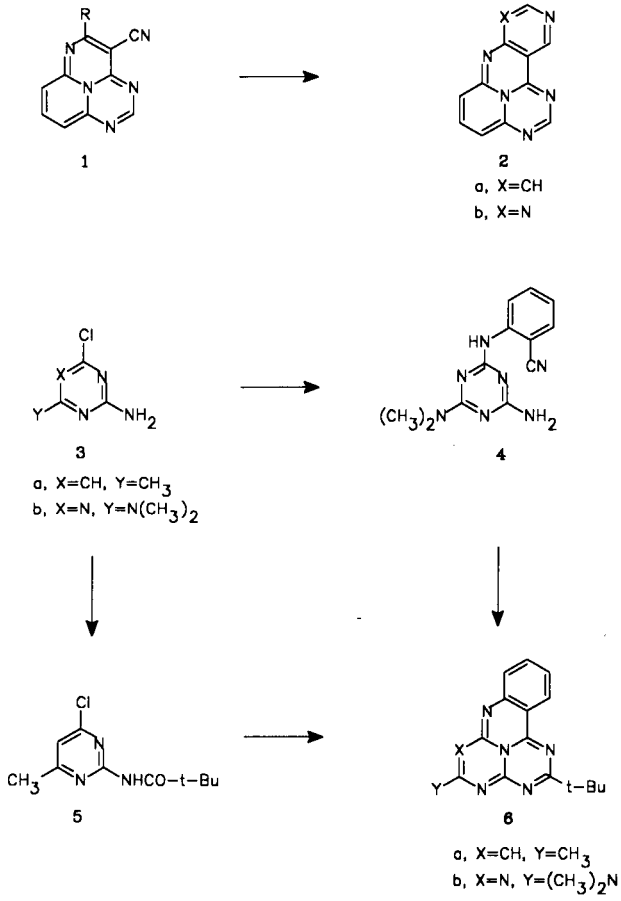

Figure 1

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 1600 spectrophotometer. The pmr spectra were determined on Varian EM-360 and EM-390 spectrometers using TMS as an internal reference. Analyses were detemined by Galbraith Laboratories, Inc., Knoxville, Tennessee. All evaporations were carried out on a rotary evaporator at reduced pressure. Silica Gel (70-230 mesh) for column chromatography was obtained from ICN Pharmaceutical Inc. Trimethylacetyl chloride, 2,6-lutidine and 2-amino-4-chloro-6-methylpyrimidine were purchased from Aldrich Chemical Company.

4-Chloro-6-methyl-2-trimethylacetamidopyrimidine (**5**).

A stirred mixture of **3a** (8.6 g, 0.06 mole), dry 2,6-lutidine (6.44 g, 0.06 mole) and dry toluene (70 ml) was warmed to effect solution and then redistilled trimethylacetyl chloride (7.24 g, 0.06 mole) was added. The lutidine salt that had formed after refluxing the reaction mixture for 2 hours was removed by suction filtration and the filtrate was evaporated to dryness. The yellow residue was recrystallized from petroleum ether (65-75°) and gave 8.03 g (59%) of yellow crystals, mp 115-120°, suitable for conversion to **6a**. The analytical sample of **5** was obtained by chromatography over silica gel using chloroform-methanol (9:1) followed by recrystallization from petroleum ether (65-75°), yellow crystals, mp 122-123°; ir (Nujol): 3287 (NH), 1694 (CO) cm^{-1}; pmr (carbon tetrachloride): δ 1.32 (s, 9H, *t*-Bu), 2.40 (s, 3H, CH_3), 6.70 (s, 1H, H_5).

Anal. Calcd. for $C_{10}H_{14}ClN_3O$: C, 52.75; H, 6.20; N, 18.45. Found: C, 52.90; H, 6.23; N, 18.62.

2-*t*-Butyl-5-methyl-1,3,4,7,11c-pentaazabenz[*de*]anthracene (**6a**).

A stirred solution of **5** (1.83 g, 0.008 mole) in dry chlorobenzene (20 ml) was treated with anthranilonitrile (1.92 g, 0.016 mole) and the mixture was refluxed for 1.75 hours. The reddish-orange solid that formed was collected by suction filtration and the filtrate "A" was set aside. The filter cake was washed successively with small amounts of chlorobenzene and low boiling petroleum ether and allowed to air dry, 1.77 g. A thin slurry of this material in 75 ml of warm (45°) methanol was treated with 0.90 ml of triethylamine. The heavy precipitate that resulted after stirring for an additional 15 minutes was collected by suction filtration. The ether-washed orange filtercake of **6a** weighed 1.18 g, mp 276-278°.

Filtrate "A" was evaporated to dryness, triturated with ether to crystallize it and the collected solid was neutralized with triethylamine as outlined above to yield 0.22 g additional **6a**, mp 276-278°, combined yield 1.40 g (60%). Recrystallization from 2-methoxyethanol gave red crystals, mp 277-278°; ir (Nujol): 3500-3200 and 2300-2100 cm^{-1}, transparent; pmr (deuteriochloroform): δ 1.20 (s, 9H, *t*-Bu), 2.02 (s, 3H, CH_3), 5.87 (s, 1H, H_6), 7.00-8.50 (m, 4H, ArH).

Anal. Calcd. for $C_{17}H_{17}N_5$: C, 70.08; H, 5.88; N, 24.04. Found: C, 70.16; H, 5.97; N, 24.10.

2-Amino-4-(2-cyanoanilino)-6-dimethylamino-*s*-triazine (**4**).

A stirred mixture of **3b** [3] (9.11 g, 0.052 mole) and anthranilonitrile (11.8 g, 0.01 mole) in 100 ml of dry 1,2-dimethoxyethane (glyme) was refluxed for 19 hours and filtered at the boil. The collected solids after washing successively with small amounts of glyme and ether were oven dried at 60° for 15 minutes. A stirred solution of the pale-yellow solid in 95 ml of methanol on treatment with 3.7 ml of triethylamine gave a difficulty stirrable slurry of crystals. Addition of 50 ml of methanol reduced the congestion; the mixture was stirred for 15 minutes more and then filtered. The filtercake was washed with ether and oven dried (60°), 5.22 g (39%), mp 212-213°. Recrystallization from glyme gave white crystals mp 212-213°; ir (Nujol): 3428, 3334, 3226 (NH), 2227 (CN) cm^{-1}; pmr (deuteriochloroform and trifluoroacetic acid): δ 3.25 (s, 6H, $(CH_3)_2N$), 7.25-7.95 (m, 4H, ArH).

Anal. Calcd. for $C_{12}H_{13}N_7$: C, 56.46; H, 5.13; N, 38.41. Found: C, 56.43; H, 5.16; N, 38.30.

2-*t*-Butyl-5-dimethylamino-1,3,4,6,7,11c-hexaazabenz[*de*]anthracene (**6b**).

A cold (6°) stirred slurry of **4** (1.4 g, 0.0055 mole), dry pyridine (0.41 g, 0.0052 mole) and dry glyme (10 ml) was treated dropwise (nitrogen atmosphere) with redistilled trimethylacetyl chloride (1.57 g, 0.013 mole). The temperature was maintained at about 6° for 15 minutes after completion of addition and the stirred mixture was then refluxed for 23 hours. The solids were collected by suction filtration at room temperature and washed successively with small amounts of glyme and ether. A stirred solution of the air-dried yellow product was dissolved in 20 ml of warm (35°) methanol and upon treatment with 0.7 ml of triethylamine a heavy precipitate formed. The yellow solid obtained after filtration of the reaction mixture was washed successively with small amounts of methanol and ether and was then chromatographed on silica gel using chloroform-ethyl acetate (1:1) as eluent. The amber fraction was collected and gave 0.57 g (32%) of an orange solid, mp 218-220°. Recrystallization from petroleum ether (110-120°) gave orange crystals mp 218-220°; ir (Nujol): 3500-3200 and 2300-2100 cm^{-1} transparent; pmr (deuteriochloroform): δ 1.4 (s, 9H, *t*-Bu), 3.27 (s, 6H, $(CH_3)_2N$), 7.20-8.42 (m, 4H, ArH).

Anal. Calcd. for $C_{17}H_{19}N_7$: C, 63.53; H, 5.96; N, 30.51. Found: C, 63.39; H, 6.09; N, 30.21.

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REFERENCES AND NOTES

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