

Synthesis of 11*H*-Indolo[2,3-*i*]phenanthridine (1)

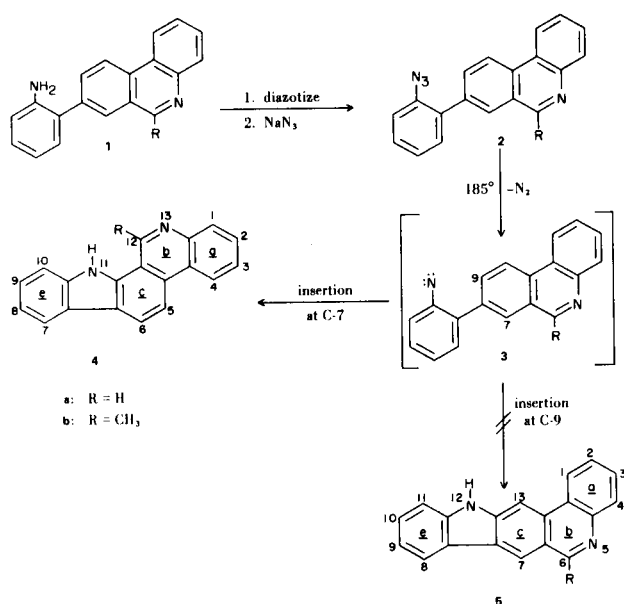
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In the synthesis of 5,12-diazadibenz[*a,h*]anthracene (4) it was found that *N*-acyl derivatives of 8-(2-amino-1-phenyl)phenanthridine (1a) fail to undergo cyclization in the presence of hot polyphosphoric acid fortified with phosphorus pentoxide, conditions which are believed to require electrophilic substitution into the phenanthridine nucleus (5). Resistance to this cyclization is probably enhanced through coordination of the phenanthridine nitrogen atom with a proton or other Lewis acid in the solvent. In an attempt to corroborate this presumption, we have now investigated cyclization of 1a under conditions which would involve both the presence of a chemically neutral solvent and an attack on the phenanthridine ring by an electrically neutral moiety. For this purpose, the diazonium derivative of 1a was treated with sodium azide in aqueous buffer to produce the solid azide 2a (Scheme 1). Thermal decomposition of 2a gave a yellow, crystalline product A (C₁₉H₁₂N₂), assigned the structure of 11*H*-indolo[2,3-*i*]phenanthridine (4a) (77%) - presumably formed *via* the intermediate nitrene 3a (6).

SCHEME 1



It is apparent that cyclization of 3a could occur by insertion into the C-H bond at either C-7 (to form 4a, as shown) or C-9 (to form isomeric 5a). Thin-layer chromatography of crude product showed only one fluorescent spot (plus highly colored byproducts), consistent with the presence of a single indolophenanthridine therein (7). The infrared spectrum of a nujol mull of A exhibited a strong doublet (at 740 and 745 cm⁻¹) for the presence of two sets of four vicinal aromatic hydrogen atoms (rings *a* and *e*), a medium band (two vicinal hydrogen atoms?) at 805, and only a weak band in the region 830-900 (where absorption for lone hydrogen atoms should occur).

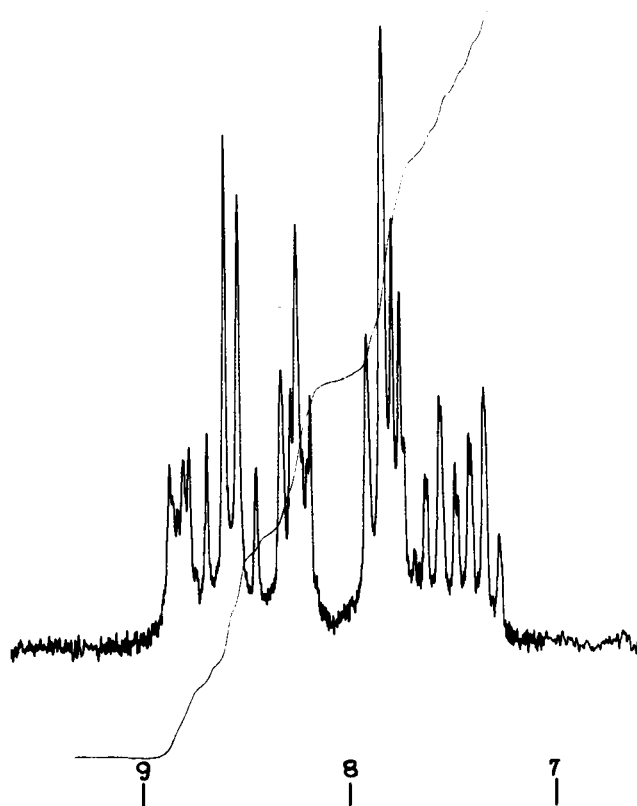
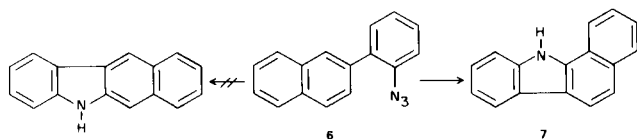


Figure 1. 100-MHz pmr spectrum of 4a in the region δ 7-9 ppm (solvent, hexadeuteriodimethyl sulfoxide).

The 100-MHz pmr spectrum of *A* consisted of four major features, two downfield singlets for one proton each at δ 12.83 and 10.20 ppm and two complex multiplets (Figure 1) for five protons each at 9.0-8.1 and 8.1-7.2. The singlet at 12.83 is assigned to the NH proton since it disappears on treatment of the sample with deuterium oxide plus sodium carbonate. The other singlet corresponds to an α -pyridinoid proton inasmuch as it disappears on successive treatment of the sample with methyl lithium (two equivalents), water, and air (oxidation). The upfield multiplet is ascribed to H-2, H-3, and H-8 to H-10 in **4a** (or to H-2, H-3, and H-9 to H-11 in **5a**). This assignment is partially corroborated by a close similarity between the spectral pattern of the 7.7-7.2 portion of this multiplet and the upfield portion of the pmr spectrum of carbazole (determined under the same conditions). From expansion of the spectrum for the downfield multiplet of *A* and careful measurements of both separations and areas of the four sharp peaks in the region 8.75-8.4 ppm, it was apparent (8) that *A* contains an AB system ($J_{AB} = 8.7$ Hz) - consistent with structure **4a** (for protons at C-5 and C-6) but not with structure **5a**.

Cyclization of 6-methyl-8-(2-amino-1-phenyl)phenanthridine (**1b**) likewise gave (albeit in much lower yield) an indolophenanthridine, to which structure **4b** was assigned. Although the doublet of doublets for the AB system was partially obscured in the expanded pmr spectrum of **4b**, the closely similar ultraviolet spectra of **4a** and **4b** (in both neutral and acidified solutions) established the presence of identical conjugated systems in both compounds.

The predominant (if not exclusive) formation of **4a** from **2a** has a precedent in the observation of Smith, Clegg, and Hall (9) that thermolysis of azide **6** gives quantitative conversion to benzo[*a*]carbazole (**7**). The nitrene from **6** undergoes insertion into the α (rather than



the β C-H bond of the naphthalene ring. Analogously, insertion in nitrene **3a** occurs at an α -type position (*i.e.* at C-7) of the phenanthridine ring. While the mechanism of cyclizations of aryl nitrenes to carbazoles is uncertain, the selective formations of **4a** and **7** find a ready interpretation in terms of a pathway which involves initial, preferential addition of the nitrene nitrogen atom to the adjacent aromatic bond of higher order (*i.e.* to the 1,2-bond, rather than the 2,3-bond, in naphthalene; to the 7,8-bond, rather than the 8,9-bond, in phenanthridine) to form an aziridine intermediate, which subsequently undergoes rearrangement to the carbazole (10).

The ultraviolet-visible absorption spectrum of **4a** in ethanol shows three strong absorption bands, all of which are shifted bathochromically in the presence of hydrochloric acid. This shift is small (2-6 nm) for the peaks at shorter wavelength, but is remarkably large (61 nm) for the long-wavelength band (at 345 nm).

EXPERIMENTAL (11)

11*H*-Indolo[2,3-*i*]phenanthridine (**4a**).

To a stirred cold (0-5°) solution of 0.276 g. of 8-(2-amino-1-phenyl)phenanthridine (**1a**) (4) in 4 ml. of 6.5 *M* hydrochloric acid was added dropwise a solution of 0.071 g. of sodium nitrite in 1 ml. of water. This solution was in turn added dropwise to a cold stirred solution of 0.065 g. of sodium azide and 0.38 g. of sodium acetate trihydrate in 6 ml. of water. The mixture was stirred one hour longer and then allowed to warm slowly to room temperature. The yellow precipitate (0.3 g.) of azide **2a** was collected by filtration and dried in air; *ir* (nujol, Beckman IR-5A) 2130 and 1300 cm^{-1} (azide) (12).

The azide was dissolved in 100 ml. of alkene-free kerosene (initial b.p. *ca.* 185°) (13) by slowly warming (with attendant evolution of nitrogen gas) to 180° over a period of *ca.* two hours (14). The yellow solution was refluxed for one hour, cooled to -15°, and filtered to collect crude **4a**. A deposit of this solid (from solution in ethanol) onto 5 g. of silica gel G was placed atop a column of plain adsorbent (30 g.) and eluted with a binary solvent which varied from 100% benzene to 100% ethyl acetate. Purified **4a** was obtained as yellow needles (0.21 g., 77% from **1a**, m.p. 285-300° dec.) from the effluent which contained 25-60% ethyl acetate. Sublimation at 165° (0.2 mm.) gave an orange-tan powder, m.p. 300-310° dec.; uv-visible max. (ethanol) 226 nm ($\log \epsilon = 4.40$) shoulder, 249 (4.65), 297 (4.67), 372 (3.85) shoulder, 387 (3.95); uv min. 268 (4.26), 345 (3.64); uv-visible max. (ethanolic hydrogen chloride) 224 nm ($\log \epsilon = 4.46$), 255 (4.53), 299 (4.55), 448 (3.96); uv min. 239 (4.37), 272 (4.23), 349 (3.42); pmr (hexadeuteriodimethyl sulfoxide, 100 MHz) δ 12.83 (s, 1, NH), 10.20 (s, 1, H-12), 8.9-8.75 (m, 1, H-4), 8.58 (d of d, 2, $J_{5,6} = 8.7$ Hz, $\Delta\delta = 12.3$ Hz, H-5 and H-6), 8.4-8.1 (m, 2, H-1 and H-7), 8.1-7.2 ppm (m, 5, H-2, H-3, and H-8 to H-10) (15).

Anal. Calcd. for $\text{C}_{19}\text{H}_{12}\text{N}_2$: C, 85.1; H, 4.5; N, 10.4. Found: C, 85.0; H, 4.7; N, 10.3.

After standing on the shelf for two years, a sample of **4a** had a m.p. of 331-337° dec.; mass spectrum, *m/e* (relative abundance), 269 (23), 268 (100, M^+), 267 (10), 134 (18, M^{++}).

Stirring 38 mg. of **4a** with 10 ml. of benzene and 10 ml. of methyl iodide for 40 hours gave 56 mg. (96%) of bright orange methiodide, m.p. 295-300° dec., raised to 301-304° on recrystallization from acetonitrile; uv max. (ethanol) 225 nm ($\log \epsilon = 4.50$), 257 (4.52), 299 (4.56); pmr (hexadeuteriodimethyl sulfoxide) δ 10.46 (s, H-12), 4.65 ppm (s, methyl), other signals obscured.

Anal. Calcd. for $\text{C}_{20}\text{H}_{15}\text{IN}_2$: C, 58.6; H, 3.7; N, 6.8. Found: C, 59.0; H, 3.6; N, 6.9.

12-Methyl-11*H*-indolo[2,3-*i*]phenanthridine (**4b**).

As in the foregoing procedure, 6-methyl-8-(2-amino-1-phenyl)phenanthridine (**1b**) was converted into yellow azide **2b**; *ir* (nujol) 2140 and 1300 cm^{-1} . This azide was heated in kerosene to 185° over a period of 6 hours, refluxed for one hour, and processed further as with **4a**. The crude solid (42%) from chromatography

was sublimed repeatedly at 165-190° (0.2 mm.) to give bright yellow crystals of **4b**, m.p. 211-214°; ir (carbon disulfide) 3520 (m, NH), 820 (w, two vicinal aromatic H?), 765 and 750 cm^{-1} (s, two sets of four vicinal aromatic H); ir (chloroform) 3520 (m, NH), 1440 and 1355 cm^{-1} (m, methyl group); uv-visible max. (ethanol) 247 nm ($\log \epsilon = 4.41$), 295 (4.64), 368 (3.79) shoulder, 384 (3.93); uv min. 267 (4.06), 337 (3.54); uv-visible max. (ethanolic hydrogen chloride) 223 nm ($\log \epsilon = 3.98$), 254 (4.38), 302 (4.52), 434 (3.93); uv min. 230 (3.83), 269 (3.97), 340 (3.42); pmr (hexadeuteriodimethyl sulfoxide, 100 MHz) δ 11.52 (s, 1, NH), 9.1-7.4 (m, including an apparent d of d at 8.77, $J_{5,6} = 8.9$ Hz, aromatic protons), 3.68 ppm (s, 3, CH_3); mass spectrum, m/e (relative abundance), 283 (24), 282 (100, M^+), 281 (11), 141 (14, M^{++}).

Anal. Calcd. for $\text{C}_{20}\text{H}_{14}\text{N}_2$: C, 85.1; H, 5.0; N, 9.9. Found: C, 84.9; H, 5.0; N, 9.8.

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- (11) Elemental analyses were performed by M-H-W Laboratories, Garden City, Michigan and by Dr. Susan Rottschaefer of this laboratory. Unless otherwise designated, infrared spectra were obtained by means of a Beckman IR-7 spectrometer; pmr spectra, by means of a Varian A-60 spectrometer (with tetramethylsilane as internal standard); ultraviolet spectra, by means of a Cary model 15 spectrometer; and mass spectra, by means of a CEC model 21-110 instrument at 70 eV. Only mass spectral peaks of relative abundance $\geq 10\%$ of the most abundant peak are reported.
- (12) N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964, pp. 206-207.
- (13) Prepared by extraction of commercial grade kerosene with concentrated sulfuric acid for one week, washing with aqueous sodium hydroxide and then water, drying with anhydrous magnesium sulfate, and finally distillation at 20 mm. pressure.
- (14) Method of P. A. S. Smith and B. B. Brown [*J. Am. Chem. Soc.*, **73**, 2435 (1951)] for conversion of 2-azidobiphenyl to carbazole.
- (15) Assignment of the H-4 signal downfield from that of H-1 is consistent with the pmr spectrum of phenanthridine in the same solvent; δ 9.45 (s, 1, H-6), 9.1-8.6 (m, 2, H-1 and H-10), 8.5-7.5 ppm (m, 6, other protons).