Synthesis of 5,12-Diazadibenz[*a,h*]anthracene (1)

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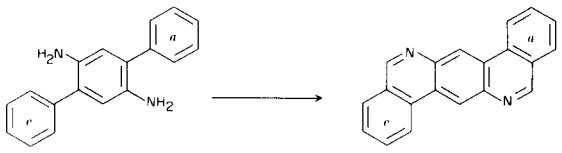
Received May 7, 1971

5,12-Diazadibenz[*a,h*]anthracene (**20**) was synthesized in 21% overall yield for seven steps. Salient features of the synthesis include the initial, one-step conversion of *trans,trans*-1,4-bis-(β-nitrovinyl)benzene into 2,2″-dinitro-*p*-terphenyl by Diels-Alder condensation plus elimination, monocyclization of the derived 2,2″-diformylamino-*p*-terphenyl to give 8-(2-amino-1-phenyl)-phenanthridine (**10**) in the presence of fortified polyphosphoric acid, and accomplishment of a second cyclization step only after reduction of the heteroring in **10** (by means of diisobutylaluminum hydride) plus formylation. The 6-methyl and 6,13-dimethyl derivatives of **20** were prepared similarly.

In a previous paper (4) we reported the synthesis of 6,13-diazadibenz[*a,h*]anthracene (**2**), an azacyclic analog of the carcinogenic hydrocarbon dibenz[*a,h*]anthracene wherein a nitrogen atom replaces one of the CH-moieties in each of the two K-regions. Used in this synthesis was the key intermediate diamine **1**. Conversion of **1** into **2** involved cyclization (of *N,N′*-diformyl-**1**) into both rings *a* and *e*, in a single step. We now describe the synthesis of an isomer of **2**, *viz.* 5,12-diazadibenz[*a,h*]anthracene (**20**), *via* the analogous key intermediate 2,2″-diamino-*p*-terphenyl (**7**) and its immediate precursor 2,2″-dinitro-*p*-terphenyl (**6**) (Scheme 1).



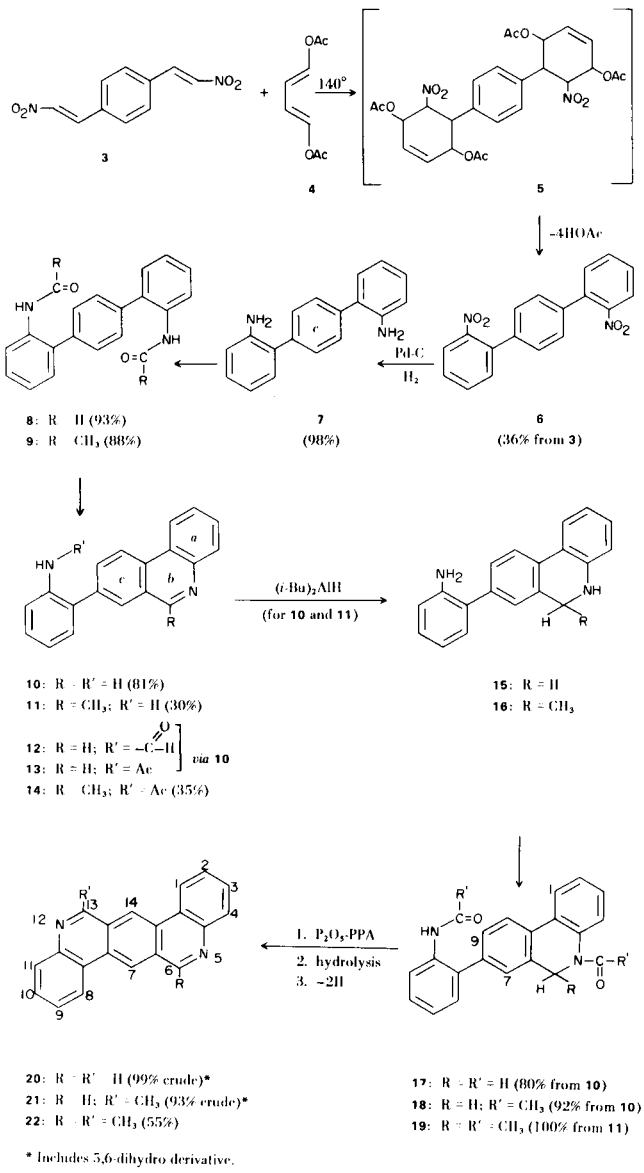
1 2

A synthesis of **6** in 1% overall yield from 2-nitrobiphenyl has been reported (5). Our first efforts to devise an improved pathway to **6** through Diels-Alder condensation of *trans,trans*-1,4-bis(β-nitrovinyl)benzene (**3**) with 1,3-butadiene failed (*vide infra*), because we were unable to effect dehydroaromatization of the adduct. This difficulty was circumvented by use of *trans,trans*-,1,4-diacetoxy-1,3-butadiene (**4**) as diene, in the manner employed by Hill and Carlson (6) with β-nitrostyrene as dienophile. Heating a mixture of **3** and **4** at 140° for 3 days produced **6** directly, presumably *via* the unstable adduct **5**. Catalytic hydrogenation of **6** to diamine **7** and acylation of **7** to amides **8** and **9** proceeded smoothly.

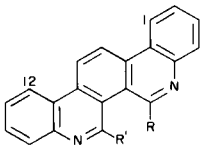
Attempts to cyclize these amides by means of fused sodium chloride-aluminum chloride (as used successfully in formation of **2**) (4) gave only tar. Monocyclization of **8** (to give **10**) and **9** (to give **11** and **14**) was effected by means of polyphosphoric acid-phosphorus pentoxide (7). However, a second cyclization step could not be accomplished by the same method on the acylamino compounds **12-14**. Apparently, the heterocyclic aromatic nitrogen atom in ring *b* of the phenanthridine nucleus markedly deactivates ring *c* toward electrophilic substitution. Competitive deacylation of the substrate then occurs and militates against the cyclization. The electronic influence of the heteroatom was altered through reduction of the C=N bond in ring *b* of **10** and **11** by means of diisobutylaluminum hydride. Thereafter, acylation of the unstable dihydro intermediate (**15** or **16**), followed by a second treatment with fortified polyphosphoric acid, did effect a second cyclization. Deacylation and dehydrogenation of the doubly cyclized product led to the desired diazadibenzanthracenes **20-22**.

It is apparent that cyclization of **17** could occur in two alternative ways, *viz.* to form **20** (as shown) or to form 5,8-diazapicene (**23**). Assignment of structure **20** to the product obtained is based primarily on the closer similarity of its ultraviolet absorption spectrum to that of dibenz-[*a,h*]anthracene than to that of picene (Fig. 1) (8). The same parent system appears to be present in **21** and **22**, which show ultraviolet spectra only slightly modified from the spectrum of **20**. In addition, the infrared spectra of **20-22** exhibit a band of medium intensity at 880 cm^{-1} (ascribed to the presence of lone aromatic hydrogens in all three compounds) (9). None of them shows strong

SCHEME I



absorption in the range 800-860 cm^{-1}, as one would expect to find if two vicinal aromatic hydrogens (as in **23-25**) were present (10). It seems likely that cyclization of **17-19** involves a transition complex between the acylamino moiety of the phenyl group and the polyphosphoric acid

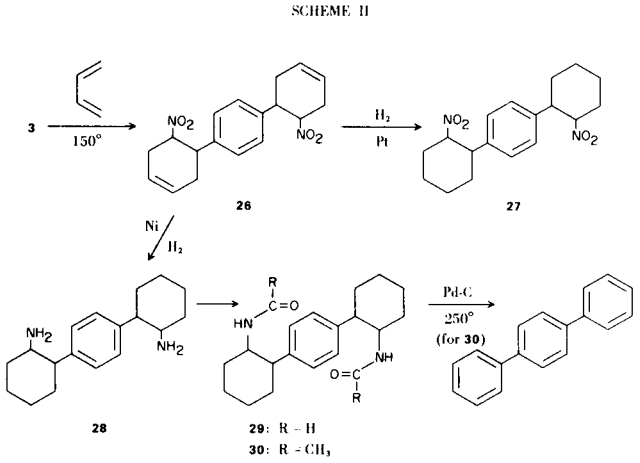


23: R = R' = H
24: R = CH_3, R' = H
25: R = R' = CH_3

reagent (in an electrophilic attack on ring *c*). Sterically, attack at C-7 should then be more facile than at C-7.

Prior to publication of the method of Hill and Carlson (6), we attempted (unsuccessfully) to prepare **20** by an alternative method. In this procedure (Scheme 2) **3** was

SCHEME II



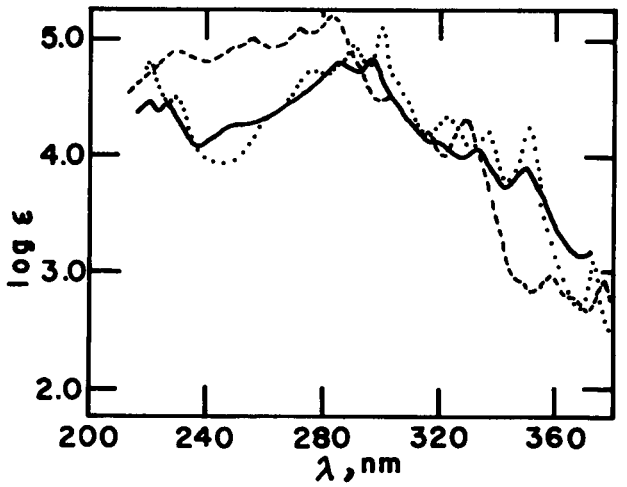


Figure 1. Ultraviolet spectra for **20** (solid line), dibenz-[*a,h*]anthracene (dotted line), and picene (broken line) (19).

first condensed with 1,3-butadiene to give dinitro compound **26**, which was hydrogenated catalytically to dinitro compound **27** and to diamine **28**. Compound **28** was easily acylated to **29** and **30**. Attempts to cyclize **30** by means of polyphosphoric acid and similar reagents gave mixtures which we were unable to separate (11). Compound **30**, in contrast to **26**, did undergo dehydrogenation in the presence of palladium-charcoal, but with attendant loss of amide substituents to give *p*-terphenyl.

EXPERIMENTAL (12)

Starting Materials.

Trans,trans-1,4-diacetoxy-1,3-butadiene (**4**) (13) [ir 1750 (C=O),

1630 (C=C), 1370 (CH_3), 955 cm^{-1} (*trans*-CH=CH); pmr δ 7.38 (d of doublets, 2, $J_{1,2} = J_{3,4} = 9$ Hz, $J_{1,3} = J_{2,4} = 3$, H-1 and H-4), 5.97 (d of doublets, 2, H-2 and H-3), 2.13 (s, 6, 2 Ac) (14)] and *trans,trans*-1,4-bis(β-nitrovinyl)benzene (**3**) (15) [ir 1635 (C=C), 1530 and 1340 (NO_2), 965 cm^{-1} (*trans*-CH=CH); pmr (DMSO-d_6) δ 8.3-7.9 (m, 4, vinyl protons), 7.97 ppm (s, 4, aromatic protons)] were prepared by reported procedures.

2,2″-Dinitro-*p*-terphenyl (**6**).

A mixture of 140 g. (0.82 mole) of **4**, 60.4 g. (0.275 mole) of **3**, and 1 g. of hydroquinone (antioxidant) was stirred in a stainless steel autoclave at 140° for 70 hours. The gummy, brown solid was extracted with boiling 20% aqueous sodium hydroxide solution for 12 hours, collected by filtration, washed with water, dried in air, and extracted exhaustively with boiling acetone. Evaporation of the acetone extract left a brown solid (40 g.) which was extracted with chloroform similarly. Concentration of this extract gave 31.5 g. (36%) of yellow solid, m.p. 227-229°, obtained as prisms on crystallization from benzene, m.p. 228-230.5°, lit (5b) m.p. 228-230.5°; uv (ethanol) 209 nm (log ε 4.40), 243 (4.42), 290 shoulder (3.55); ir 1530 and 1360 cm^{-1} (NO_2); pmr (DMSO-d_6) δ 7.57 (s, 4, protons on central ring) which is superimposed on 8.3-7.3 ppm (m, 12 total).

Anal. Calcd. for $C_{18}H_{12}N_2O_4$: C, 67.5; H, 3.8; N, 8.7. Found: C, 67.7; H, 3.8; N, 8.4.

From the chloroform mother liquors was obtained 1.6 g. (85%) of anthraquinone, m.p. 279-281°, identified by direct comparison with an authentic sample.

2,2″-Diamino-*p*-terphenyl (**7**).

A warm solution of 3 g. of 2,2″-dinitro-*p*-terphenyl in 25 ml. of glacial acetic acid and 135 ml. of benzene was agitated with 0.1 g. of 30% palladium-on-charcoal in the presence of hydrogen gas at 1 atm. pressure for 24 hours, whereupon hydrogen uptake ceased. The catalyst was removed by filtration and the filtrate was brought to *p*H 11 with aqueous sodium hydroxide solution. The organic layer, combined with benzene extracts of the aqueous layer, was dried and evaporated to leave 2.37 g. (98%) of solid, obtained as needles on sublimation at 180° (0.5 mm.), m.p. 204.5-205.5°; uv (ethanol) 211 nm (log ε 4.77), 223 shoulder (4.64), 307 (4.06); uv (ethanolic hydrogen chloride) 209 nm (log ε 4.78), 249 (4.47); ir 3490 and 3390 cm^{-1} (NH_2); pmr δ 7.55 (s, 4, protons on central ring), 7.4-6.4 (m, 8, aromatic protons on end rings), 3.80 (broad s, 4, 2 NH_2).

Anal. Calcd. for $C_{18}H_{16}N_2$: C, 83.0; H, 6.2; N, 10.8. Found: C, 83.1; H, 6.3; N, 11.0.

2,2″-Diformylamino-*p*-terphenyl (**8**).

A solution of 1.23 g. of 2,2″-diamino-*p*-terphenyl in 25 ml. of anhydrous formic acid was refluxed for 20 hours in a nitrogen atmosphere. Slow distillation of excess solvent left a solid which was sublimed at 245° (0.5 mm.) to yield 1.39 g. (93%) of prisms, m.p. 295-296.5°; ir (nujol) 3220 (NH), 1690 and 1660 cm^{-1} (amide C=O); pmr (CF_3CO_2H) δ 9.4-8.3 (m, NHCHO), 7.55 ppm (broad s, aromatic protons).

Anal. Calcd. for $C_{20}H_{16}N_2O_2$: C, 75.9; H, 5.1; N, 8.9. Found: C, 76.2; H, 5.2; N, 9.1.

2,2″-Diacetylamino-*p*-terphenyl (**9**).

Stirring 0.5 g. of 2,2″-diamino-*p*-terphenyl with 4 ml. of acetic anhydride for one hour at room temperature gave 0.59 g. (88%) of tan solid (m.p. 210-220°), obtained as needles on crystallization from ethanol, m.p. 230.5-232°; uv (ethanol) 212 nm (log ε 5.04), 248 shoulder (4.75); ir (nujol) 3400 (NH), 1660 cm^{-1} (amide C=O); pmr (DMSO-d_6) δ 9.21 (s, 2, 2 NH), 7.48 (s, protons on central ring) superimposed on 7.9-7.1 (m, 12 total, aromatic protons), 1.93 ppm (s, 6, 2 Ac).

Anal. Calcd. for $C_{22}H_{20}N_2O_2$: C, 76.7; H, 5.9; N, 8.1. Found: C, 77.0; H, 6.0; N, 8.0.

8-(2-Amino-1-phenyl)phenanthridine (**10**).

To a clear solution (from preheating and stirring) of 5 g. of phosphorus pentoxide in 75 g. of polyphosphoric acid at 120° in an atmosphere of nitrogen was added 2.03 g. of amide **8**. The mixture was heated at 145° for 3-5 hours and then poured onto 600 g. of ice. The hydrolysate was stirred for 5 hours, basified by dropwise addition of concentrated ammonium hydroxide, stirred 12 hours, and extracted with benzene. Concentration of the dried extract gave 1.4 g. (81%) of solid, m.p. 169-170.5°, raised to 170-171° on crystallization from ethyl acetate and sublimation at 120° (0.05 mm.); uv (ethanol) 217 nm (log ε 4.31), 254 (4.62), 299 shoulder (4.05), 313 shoulder (3.86); ir 3490 and 3390 cm^{-1} (NH); pmr δ 9.25 (s, 1, H-6), 8.7-6.7 (m, other aromatic protons), 3.80 ppm (broad s, 2, NH_2).

Anal. Calcd. for $C_{19}H_{14}N_2$: C, 84.4; H, 5.2; N, 10.4. Found: C, 84.3; H, 5.4; N, 10.5.

8-(2-Formylamino-1-phenyl)phenanthridine (**12**).

A mixture of 0.2 g. of amine **10** and 12 ml. of acetic-formic anhydride (16) was stirred at 0-5° for 18 hours. The solvent was removed and the residue was basified with ammonium hydroxide to give a tan solid, m.p. 174-178°, raised to 182.5-183.5° on recrystallization from acetone-petroleum ether (30-60°); uv (ethanol) 217 nm (log ε 4.17), 259 (4.59), 335 (3.14); uv (ethanolic hydrogen chloride) 253 nm (log ε 4.49), 270 (4.51), 310 shoulder (3.97); ir 3400 (NH), 1680 cm^{-1} (amide C=O); pmr (DMSO-d_6) δ 9.49 (broadened s, 2, H-6 plus CHO), 9.2-7.3 ppm (m, 12, NH plus other aromatic protons).

The *N-benzyl bromide salt* was prepared by stirring and refluxing a mixture of 0.4 g. of crude **12**, 4 ml. of benzyl bromide, and 50 ml. of benzene for 8 hours. The cooled solution deposited 0.63 g. (quantitative yield) of yellow prisms, m.p. 229-231° after crystallization from ethanol (charcoal); ir (nujol) 1680 cm^{-1} (amide C=O); pmr (DMSO-d_6) δ 10.89 (broadened s, 1, H-6), 9.82 (broadened s, 1, CHO), 9.5-7.1 (m, NH plus other aromatic protons), 6.56 ppm (broadened s, 2, benzylic CH_2).

Anal. Calcd. for $C_{27}H_{21}BrN_2O$: C, 69.1; H, 4.5; Br, 17.0; N, 6.0. Found: C, 69.0; H, 4.6; Br, 17.2; N, 6.0.

8-(2-Acetylamino-1-phenyl)phenanthridine (**13**).

The precipitate which formed on stirring 0.355 g. of amine **10** with 15 ml. of acetic anhydride for 36 hours was collected by filtration, washed with water, and dried; yield 0.276 g. (67%) m.p. 195-197°, raised to 201.5-202.5° by crystallizations from acetone; ir 3430 (NH), 1680 cm^{-1} (amide C=O); pmr δ 9.08 (broad s, H-6), 8.7-7.0 (m, NH plus other aromatic protons), 2.02 ppm (s, Ac).

Anal. Calcd. for $C_{21}H_{16}N_2O$: C, 80.7; H, 5.2; N, 9.0. Found: C, 80.8; H, 5.3; N, 9.0.

Cyclization of 2,2″-Diacetylamino-*p*-terphenyl.

Treatment of 1.46 g. of amide **9** with phosphorus pentoxide and polyphosphoric acid in the manner used to prepare amine **10** gave 1.18 g. of crude product, separated into two components by means of preparative tlc on silica gel G (90 g., 1.25 mm. thickness) with ethyl acetate as eluent. The leading zone (R_f = 0.6) furnished 0.36 g. (30%) of 6-methyl-8-(2-amino-1-phenyl)phenanthridine (**11**), while the trailing zone (R_f = 0.3) produced 0.48 g. (35%) of 6-

methyl-8-(2-acetylamino-1-phenyl)phenanthridine (**14**).

Sublimation of amine **11** at 140° (0.1 mm.) gave yellow needles (m.p. 178-180°), purified further by chromatography and crystallizations (platelets) from petroleum ether-benzene, m.p. 183-184°; uv (ethanol) *ca.* 213 nm (log ϵ 4.58), 245 shoulder (4.61), 253 (4.65), 302 shoulder (4.03); uv (ethanolic hydrogen chloride) 257 nm (log ϵ 4.69), 266 shoulder (4.62), 314 shoulder (3.78); ir 3500 and 3400 cm^{-1} (NH); pmr δ 8.9-6.8 (m, aromatic protons), 3.78 (broad s, 2, NH_2), 3.05 ppm (s, 3, CH_3).

Anal. Calcd. for $C_{20}H_{16}N_2$: C, 84.5; H, 5.7; N, 9.8. Found: C, 84.3; H, 5.8; N, 9.8.

Sublimation of amide **14** at 150° (0.1 mm.) gave a solid (m.p. 197.5-199.5°) which formed faintly yellow prisms on crystallization from benzene, m.p. 201.5-203°; uv (ethanol) 217 nm (log ϵ 4.26), 262 (4.61); ir 3450 (NH), 1680 cm^{-1} (amide C=O); pmr δ 9.0-7.3 (m, 12, aromatic protons plus NH), 2.97 (s, 3, Ac), 2.02 ppm (s, 3, CH_3 at C-6).

Anal. Calcd. for $C_{22}H_{18}N_2O$: C, 81.0; H, 5.6; N, 8.6. Found: C, 81.2; H, 5.7; N, 8.7.

In a separate experiment 1.85 g. of amide **9** was heated for 18 hours and the crude product was hydrolyzed by refluxing with 50 ml. of 20% aqueous sulfuric acid for 8 hours. The reaction mixture was basified with sodium hydroxide and filtered; yield 1.12 g. (73%) of amine **11** (after purification by chromatography on silica gel G).

8-(2-Amino-1-phenyl)-5,6-dihydrophenanthridine (**15**).

To a stirred solution of 0.135 g. (0.5 mmole) of amine **10** in 20 ml. of anhydrous benzene in a nitrogen atmosphere was added dropwise 1.35 ml. of a 20% (by weight) solution of diisobutylaluminum hydride (16 mmoles) (Texas Alkyls, Deer Park, Texas) in benzene. The orange color that originally appeared changed to yellow and evolution of hydrogen ceased after 5 minutes. The solution was stirred for one hour at room temperature and then hydrolyzed slowly by the dropwise addition of aqueous tetrahydrofuran (3% water, by volume) until a gelatinous precipitate formed. The liquid phase was separated, combined with a benzene-acetone (1:1 by volume) extract of the precipitate, dried with anhydrous magnesium sulfate, and evaporated *in vacuo* to give **15** as a slightly yellow solid; uv (ethanol) 243 nm (log ϵ 4.33); uv (ethanolic hydrogen chloride) 278 nm (log ϵ 4.36); ir 3500 and 3410 cm^{-1} (NH); pmr (hexadeuteriobenzene) 7.8-6.2 (m, aromatic protons), 3.91 (s, 2, N-CH_2), 3.14 ppm (broad s 3, NH and NH_2).

Since **15** was readily susceptible to air oxidation it was immediately acylated to **17** or **18** for storage and further use.

5-Formyl-8-(2-formylamino-1-phenyl)-5,6-dihydrophenanthridine (**17**).

The crude amine **15**, prepared from 0.505 g. of **10**, was stirred with 25 ml. of acetic-formic anhydride for 12 hours at 0°. Removal of excess reagent *in vacuo* left 0.49 g. (80%) of **17** (m.p. 241-242.5°), obtained as white prisms on crystallization from acetone, m.p. 242-243°; uv (ethanol) 246 nm (log ϵ 4.38), 286 (4.29); ir (nujol) 3300 (NH), 1680 and 1650 cm^{-1} (2 amide C=O); pmr (DMSO-d_6) δ 9.46 (broad signal, 1, NHC*H*O), 8.75 (s, 1, CH_2NCHO), 8.4-7.2 (2m, 12, NH and aromatic protons), 4.94 ppm (broadened s, N-CH_2).

Anal. Calcd. for $C_{21}H_{16}N_2O_2$: C, 76.8; H, 4.9; N, 8.5. Found: C, 76.8; H, 4.9; N, 8.3.

5-Acetyl-8-(2-acetylamino-1-phenyl)-5,6-dihydrophenanthridine (**18**).

Stirring the crude amine **15**, prepared from 0.135 g. of **10**, with 15 ml. of acetic anhydride for 18 hours at room temperature and then concentration of the solution gave 0.163 g. (92%) of **18** (m.p. 193.5-195°), obtained as cream-colored needles on crystallization from acetone; m.p. 193.5-194.5°; uv (ethanol) 246 nm (log ϵ 4.27), 287 (4.30); ir 3440 (NH), 1690 and 1660 cm^{-1} (2 amide C=O); pmr (DMSO-d_6) δ 9.28 (broadened s, 1, NH), 8.1-7.2 (m, 11, aromatic protons), 4.88 (broadened s, 2, N-CH_2), 2.17 and 1.91 (2 s, 3 each, 2 Ac).

Anal. Calcd. for $C_{23}H_{20}N_2O_2$: C, 77.5; H, 5.7; N, 7.9. Found: C, 77.8; H, 5.8; N, 7.7.

5-Acetyl-6-methyl-8-(2-acetylaminophenyl)-5,6-dihydrophenanthridine (**19**).

In the preceding manner 1 g. of amine **11** was converted into 6-methyl-8-(2-amino-1-phenyl)-5,6-dihydrophenanthridine (**16**), obtained as a yellow liquid; ir 3480 and 3380 cm^{-1} (NH); pmr (C_6D_6) δ 7.7-6.2 (m, aromatic protons), 4.15 (q, J = 6.3 Hz, H-6), 3.30 (broad s, NH_2 and NH), 1.07 ppm (d, CH_3 at C-6).

The crude **16** was stirred with acetic anhydride as in the synthesis of **18**. The residue from evaporation of the reaction mixture was brought to *p*H 8 with aqueous sodium bicarbonate solution and extracted with chloroform. Evaporation of the chloroform left 1.38 g. (quantitative yield) of tan solid, m.p. 90-95°. Repetitive crystallizations from ether gave faintly cream-colored prisms of **19**, m.p. 173-174°; uv (ethanol) 247 nm (log ϵ 4.44), 287 (4.39); ir 3420 (NH), 1680 and 1630 cm^{-1} (2 amide C=O); pmr δ 8.3-7.7 (m, 3, NH plus 2 aromatic protons), 7.5-7.1 (m, 9, other aromatic protons), *ca.* 6.00 (broad signal, 1, H-6), 2.20 and 2.01 (2 s, 3 each, 2 Ac), 1.22 ppm (d, 3, J = 7 Hz, CH_3 at C-6). Double irradiation of **19** at 6.00 ppm (Varian HA-100 instrument) caused collapse of the doublet at 1.22 to a singlet.

Anal. Calcd. for $C_{24}H_{22}N_2O_2$: C, 77.8; H, 6.0; N, 7.6. Found: C, 77.9; H, 5.8; N, 7.4.

5,12-Diazadibenz[*a,h*]anthracene (**20**).

A stirred mixture of 0.728 g. of amide **17**, 150 g. of polyphosphoric acid, and 2 g. of phosphorus pentoxide was warmed slowly at 140° and held at this temperature for 6 hours, whereupon a yellow fluorescence was apparent. The mixture was poured onto ice, stirred, and basified to *p*H 11 with ammonium hydroxide. The yellow precipitate (0.62 g.) which formed appeared, by ir and nmr analysis, to be a 3:2 mixture of **20** and its dihydro derivative (99% crude yield). A solution of the precipitate in 75 ml. of benzene was refluxed with 0.1 g. of 30% palladium-on-charcoal in the presence of air for 12 hours. Cooling the benzene solution gave **20**, purified by sublimation at 160° (0.05 mm.) plus recrystallizations from ethanol and benzene, obtained as yellow needles, m.p. 320-321.5° (sealed tube); uv (ethanol) 221 nm (log ϵ 4.43), 227 (4.42), 251 shoulder (4.25), 286 (4.81), 297 (4.82), 317 shoulder (4.13), 333 (4.01), 350 (3.89); uv (ethanolic hydrogen chloride) 233 nm (log ϵ 4.27), 262 (4.40), 292 (4.64), 305 (4.63), 363 (3.95); ir (nujol) 880 (lone aromatic H), 750 cm^{-1} (4 vicinal aromatic H); pmr (CF_3CO_2H) δ 10.32 and 10.26 (2 s, *ca.* 2 each, H-6 and H-13; H-7 and H-14), 9.5-9.0 (m, 2, H-1 and H-8), 8.8-8.0 ppm (m, 6, H-2 to H-4, H-9 to H-11); mass spectrum (17), m/e (relative abundance), 281 (25), 280 (100), 279 (9), 140 (12, M^{++}), 78 (31, probably benzene of crystallization).

Anal. Calcd. for $C_{20}H_{12}N_2$: C, 85.7; H, 4.3; N, 10.0. Found: C, 85.7; H, 4.7; N, 9.9.

6-Methyl-5,12-diazadibenz[*a,h*]anthracene (**21**).

A. Cyclization with Polyphosphoric Acid.

In the manner used for the preparation of **20** 0.589 g. of amide **18** was refluxed with fortified polyphosphoric acid for 8 hours, whereupon a yellow-green fluorescence (considered to indicate completion of the cyclization) was noted. The mixture was pro-

cessed in the foregoing manner except that concentration of the benzene extract gave 0.159 g. (32%) of yellow crystals of the intermediate 6-methyl-12,13-dihydro-5,12-diazadibenz[*a,h*]anthracene (**21a**); pmr (DMSO-d_6) δ 8.49 and 8.41 (2s, H-7 and H-14), 8.1-6.5 (m, other aromatic protons), 6.17 (broad s, NH), 4.60 (broadened s, N-CH_2), 3.01 ppm (s, CH_3).

Evaporation of the benzene mother liquors gave 0.295 g. (61%) of crystalline **21**, purified further by sublimation at 155° (0.05 mm.) and recrystallization from benzene to give light tan prisms, m.p. 273.5-275° (sealed tube); uv (ethanol) 222 nm (log ε 4.53), 226 shoulder (4.50), 249 (4.18), 268 shoulder (4.32), 288 (4.79), 298 (4.82), 318 shoulder (4.12), 333 (3.98), 350 (3.81); uv (ethanolic hydrogen chloride) 232 nm (log ε 4.40), 263 (4.37), 293 (4.64), 306 (4.68), 364 (3.98); ir (nujol) 880 (lone aromatic H), 755 and 745 cm^{-1} (two sets of 4 vicinal aromatic H); pmr (CF_3CO_2H) 10.35, 10.30, and 10.27 (3 overlapping s, 3, H-7, H-13, H-14), 9.4-9.1 (m, 2, H-1, H-8,), 8.7-8.1 (m, 6, H-2 to H-4, H-9 to H-11), 3.83 ppm (s, 3, CH_3).

Anal. Calcd. for $C_{21}H_{14}N_2$: C, 85.7; H, 4.8; N, 9.5. Found: C, 85.9; H, 5.0; N, 9.1.

Dehydrogenation of the preceding dihydro intermediate with palladium-on-charcoal and benzene gave additional **21**.

B. Cyclization with Polyphosphate Ester.

A solution of 0.3 g. of amide **18** in 35 g. of polyethyl metaphosphate (18) was heated at 115° for 6 hours. The mixture was cooled and added to 30 ml. of 15% aqueous sulfuric acid. This mixture was heated at 80° for 3 hours, poured into water, and basified; yield 0.179 g. (72%) of **21a**, identical with product obtained in part A.

6,13-Dimethyl-5,12-diazadibenz[*a,h*]anthracene (**22**).

In the same manner as used to prepare **20**, 0.5 g. of amide **19** was cyclized (10 hours heating) and dehydrogenated. From the benzene solution there resulted only 39 mg. of crystalline **22**, obtained as yellow needles on recrystallizations from benzene and ethanol, m.p. 314.5-316° (sealed tube); uv (ethanol) 223 nm (log ε 4.42), 250 (4.13), 268 shoulder (4.29), 288 (4.79), 299 (4.82), 321 (4.12), 335 (4.00), 352 (3.81); uv (ethanolic hydrogen chloride) 233 nm (log ε 4.24), 264 (4.36), 294 (4.65), 306 (4.70), *ca.* 367 (3.98); ir (nujol) 885 (lone aromatic H), 755 cm^{-1} (4 vicinal aromatic H); pmr (CF_3CO_2H) δ 10.17 (s, 2, H-7, H-14), 9.3-8.9 (m, 2, H-1, H-8), 8.4-8.0 (m, 6, H-2 to H-4, H-9 to H-11), 3.79 ppm (s, 6, 2 CH_3).

Anal. Calcd. for $C_{22}H_{16}N_2$: C, 85.7; H, 5.2; N, 9.1. Found: C, 85.5; H, 5.5; N, 8.9.

Extraction of the palladium-on-charcoal catalyst plus residue (from the preceding dehydrogenation) with trifluoroacetic acid and neutralization of the extract with aqueous sodium bicarbonate gave an additional 198 mg. (55% total yield) of **22**.

1,4-Bis(2-nitro-4-cyclohexen-1-yl)benzene (**26**).

A mixture of 2.8 g. of **3**, 8 ml. of 1,3-butadiene, 20 ml. of toluene, and a small amount of hydroquinone was heated at 150° for 6 hours. From the cooled reaction mixture precipitated 2.02 g. (49%) of brown crystals, m.p. 205-210°, converted to colorless prisms on recrystallizations from ethyl acetate, m.p. 230.5-232°; ir (nujol) 1550 and 1380 (NO_2), 840 cm^{-1} (*p*-disubstituted benzene); pmr δ 7.17 (s, 4, aromatic protons), 5.74 (broad pseudo-doublet, 4, 2 CH=CH), 4.99 and 4.81 (2 overlapping t, 2 total, J = 8 Hz, 2 $CHNO_2$), 3.43 and 3.32 (2 overlapping t, J = 11 Hz, 2 $CH_2CHCHNO_2$), 2.9-2.1 ppm (m, 8, 4 CH_2).

Anal. Calcd. for $C_{18}H_{20}N_2O_4$: C, 65.8; H, 6.1; N, 8.5. Found: C, 66.0; H, 6.1; N, 8.6.

1,4-Bis(2-nitro-1-cyclohexyl)benzene (**27**).

A suspension of 1 g. of **26** and 0.25 g. of platinum oxide catalyst in 150 ml. of benzene was shaken for 2 hours in the presence of hydrogen gas at 3 atm. pressure. Removal of catalyst and solvent left 0.98 g. (97%) of **27**, m.p. 232-236°, raised to 248.5-249° on recrystallizations from ethyl acetate to form prisms; ir (nujol) 1525 and 1360 (NO_2), 825 cm^{-1} (*p*-disubstituted benzene); pmr δ 7.14 (s, 4, aromatic protons), 4.9-4.0 (m, 2, 2 $CHNO_2$), 3.4-2.6 (m, 2, $2CH_2CHCHNO_2$), 2.6-1.2 ppm (m, 16, 8 CH_2).

Anal. Calcd. for $C_{18}H_{24}N_2O_4$: C, 65.0; H, 7.3; N, 8.4. Found: C, 65.3; H, 7.5; N, 8.3.

1,4-Bis(2-amino-1-cyclohexyl)benzene (**28**).

Repetition of the preceding experiment but with ethanol as solvent, 2 g. of Raney nickel catalyst, and 4 hours reaction time gave 0.84 g. (quantitative yield) of crystals. Recrystallizations from cyclohexane and petroleum ether (30-60°) gave **28** as cream-colored prisms, m.p. 133-134°; ir (3390 (NH_2), 825 cm^{-1} (*p*-disubstituted benzene); pmr δ 7.18 (s, 4, aromatic protons), 3.1-2.5 (m, 2, 2 $CH_2CHCHNH_2$), 2.5-1.1 (m, 18, 8 CH_2 + 2 $CHNH_2$), 1.0 ppm (s, 4, 2 NH_2).

Anal. Calcd. for $C_{18}H_{28}N_2$: C, 79.4; H, 10.4; N, 10.3. Found: C, 79.0; H, 10.7; N, 10.1.

1,4-Bis(2-formylamino-1-cyclohexyl)benzene (**29**).

A solution of 0.48 g. of amine **28** in 5 ml. of 98% formic acid was refluxed for 5 hours and then evaporated. The residue was triturated with ethanol to leave a white powder. Crystallization from dimethylformamide gave 0.38 g. (66%) of **29** as prisms, m.p. 296-297.5° dec.; ir (nujol) 3310 (NH), 1640 (amide C=O), 825 cm^{-1} (*p*-disubstituted benzene).

Anal. Calcd. for $C_{20}H_{28}N_2O_2$: N, 8.5. Found: N, 8.4.

1,4-Bis(2-acetylamino-1-cyclohexyl)benzene (**30**).

A mixture of 0.36 g. of amine **28** and 5 ml. of acetic anhydride was heated on a steam bath for 15 minutes. Removal of solvent gave a colorless residue (quantitative yield), crystallized as needles from ethanol, m.p. 297.5-298.5°; ir (nujol) 3280 (NH), 1630 (amide C=O), 825 cm^{-1} (*p*-disubstituted benzene); pmr δ 7.12 (s, 4, aromatic protons), 2.7-0.6 ppm (m, 28, other protons including singlet at 1.66 for *ca.* 6H in 2 Ac).

Anal. Calcd. for $C_{22}H_{32}N_2O_2$: C, 74.1; H, 9.1; N, 7.9. Found: C, 73.8; H, 9.0; N, 7.8.

Conversion of **30** to *p*-Terphenyl.

A mixture of 0.46 g. of amide **30** and 1.7 g. of 10% palladium-on-charcoal was heated at 250° for 20 hours. The residue was extracted with hot benzene. Removal of the solvent left 0.23 g. (77%) of *p*-terphenyl, m.p. 208-210°, identified by comparison with an authentic sample.

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