respectively. No unreacted aziridine could be detected after these prolonged reactions at high temperature.

Reversibility of the Thermal Valence Isomerization of 1-Cyclohexyl-6-(cyclohexylimino)-1a-phenylindano[1,2-b]aziridine. A. Reaction in the Absence of Dipolarophile.—A deoxygenated solution of 1.15 g (3 mmol) of **4** in 30 ml of toluene was heated to 135–145° for 24 hr giving a deep red color. Evaporation of the solvent and trituration of the residue with ethanol gave recovered indano[1,2-b]aziridine **4** as a slightly yellow solid, mp 158–159°, 0.702 g (61% recovery). Evaporation of the ethanol mother liquor afforded 0.068 g (19%) of **28**, 123–124°.

B. Parallel Reaction in the Presence of a Dipolarophile.—A similar experiment was performed with 1.5 g (3 mmol) of **4** and 0.519 g (3 mmol) of *N*-phenylmaleimide under exactly comparable conditions and resulted in the isolation of adduct **6** (see above), 1.34 g (80%), mp 235–236°, but no aziridine **4** could be recovered.

Reversibility of Photochemical Valence Isomerization of 1-Cyclohexyl-6-(6-cyclohexylimino)-1a-phenylindano[1,2-b]aziridine—A solution of 1.063 g (2.8 mmol) of the indano[1,2-b]aziridine **4** in 100 ml of tetrahydrofuran was irradiated under nitrogen at 0 to −10° in a quartz cell using a 450-W Hanovia high-pressure lamp for 8 hr. A deep red solution was obtained[24] and when exposed to visible light the color rapidly faded to a pale yellow resulting in a virtually complete restoration of the infrared absorption spectrum of the original compound **4**.

Photochemical Reaction between 1-Cyclohexyl-6-(cyclohexylimino)-1a-phenylindano[1,2-b]aziridine and Cyclohexylamine Hydrobromide.—A mixture of 1.15 g (3 mmol) of the indano[1,2-b]aziridine **4** and 1.08 g (6 mmol) of cyclohexylamine hydrobromide in 150 ml of ether and 20 ml of methanol was irradiated for 8 hr under nitrogen with a 450-W high-pressure Hanovia lamp in a quartz reaction vessel. The resulting yellow solid **29** was collected and recrystallized from ether–methanol, 0.527 g (38%): mp 298–299°; ir ($CHCl_3$) 1617 (C=N), 3230 cm^{-1} (NH); nmr δ_{TMS} ($CDCl_3$) 0.6–2.4 (m, 20, C_6H_{11}), 3.0–3.6 (m, 1, CHNHC=), 3.9–4.5 (m, 1, $=N^+CH$), 6.8–8.1 (m, 9, aromatic protons), 8.51 (d, 1, D_2O exchangeable NH), 9.65 (d, 1, J = 7 Hz, aromatic protons); uv_{max} (95% EtOH–HBr) 393 mμ (log ε 4.12), 335 (3.77), 324 (sh, 3.72), 288 (3.86), 279 (3.89); mass spectrum (70 eV) 384.

Anal. Calcd for $C_{27}H_{33}N_2Br$: N, 6.02. Found: N, 5.56.

The identical compound was obtained by heating the indano[1,2-b]aziridine with cyclohexylamine hydrobromide or ammonium bromide in toluene.

Photochemical Reaction between 1-Cyclohexyl-6-(cyclohexylimino)-1a-phenylindano[1,2-b]aziridine and *cis*-1,2-Dichloromethylene.—A mixture of 1.15 g (3 mmol) of the indano[1,2-b]aziridine **4** and 20 ml of *cis*-1,2-dichloroethylene in 100 ml of absolute ether was irradiated under nitrogen at 0 to 10° in a quartz reaction vessel for 8 hr. The resulting yellow solid was collected and purified by recrystallization from methanol–ether, 1.08 g (86%): mp 283–285°; ir ($CHCl_3$) 1618 (C=N), 3220 cm^{-1} (NH); nmr δ_{TMS} ($CDCl_3$) 0.7–2.5 (m, 20, C_6H_{11}), 3.3–3.7 (m, 1, =CNHCH), 4.1–4.5 (m, 1, $=^+NCH$), 7.1–8.2 (m, 9, aromatic protons), 8.54 (d, 1, D_2O exchangeable, NH), 8.68 (d, 1, J = Hz, aromatic proton); uv_{max} (95% EtOH) 222 mμ (log ε 4.59), 278 (3.66), 288 (3.64), 324 (sh, 3.47), 334 (3.55), 393 (3.99); mass spectrum (70 eV) 384.

Anal. Calcd for $C_{27}H_{33}N_2Cl$: N, 6.66. Found: N, 6.55.

The identical compound was obtained by heating the indano[1,2-b]aziridine with ammonium chloride in toluene.

Registry No.—**6a**, 27409-74-1; **6b**, 28443-72-3; **8**, 28443-73-4; **9a**, 27284-06-6; **13**, 28443-75-6; **14**, 28443-76-7; **15**, 28443-77-8; **19a**, 28443-78-9; **19b**, 28443-79-0; **20**, 28443-80-3; **21a**, 28443-81-4; **21b**, 28443-82-5; **22**, 28443-83-6; **23b**, 28443-84-7; **24**, 28443-85-8; **25a**, 28443-86-9; **25b**, 28443-87-0; **26**, 28443-88-1; **27**, 28443-89-2; **28**, 28443-90-5; **29** (X = Br), 28443-91-6; **29** (X = Cl), 28443-92-7; **30**, 28443-93-8.

(24) The very close similarity of the absorption spectrum of this species [λ_{max} (dioxane) 500 mμ, 520 (sh), 565 (sh)] to that obtained by heating **4** [λ_{max} (xylene) 505 mμ, 534 (sh), and 570 (sh)] may be noted.

Aromatic Demethoxylation in the Cyclization of 3-(β-Dialkoxyarylethylamino)phthalides to 2,3-Dihydro-7*H*-dibenzo[*de*,*h*]quinolines

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Whereas polyphosphoric acid cyclization of β-phenylethylaminophthalide (**1a**) gives lactam **3**, similar cyclizations of methylenedioxyphenyl (**1c**) and dimethoxyphenyl (**1b**) analogs proceed in the direction of respective 5,6-dialkoxy-2,3-dihydro-7-dibenzo[*de*,*h*]quinolones (**4**). In **1b** closure, the 6-methoxy group in the tetracyclic base is partly demethylated and for the most part lost, giving **4a** as the major product, together with monophenolic congener. Structure **4a** was established by spectral data, aromatization to **5**, and reduction to basic carbinol **6**, in turn further characterized as acetates **7** and **8**.

Closures of cyclic carbinolamides or enamides leading to 1-substituted (or spiro) tetrahydroisoquinoline or β-carboline acid derivatives or lactams played a prominent role in the chemistry of erythroidines[1-3] and are now well known.[4-9] These and other Pictet–Spengler closures of *N*-(β-arylethyl)enamines being our point of departure, we examined cyclizations of condensation products **1** obtained from typical primary β-arylethylamines and phthalaldehydic acid under mild conditions (azeotropic reflux, benzene or toluene).

In the first place, such products of the reaction of phthalaldehydic acid with primary amines, like those formed with secondary amines and other nucleophiles,[10] are for the most part aminophthalides **1** rather than hydroxyphthalimidines. This is apparent from their infrared spectra, in which lactone bands (5.70 μ) predominate. Further evidence for structure **1** is the fact that mild hydrogenation of **1b** and **1c** gives amino acids **2b** and **2c**, respectively, products which would not arise from hydroxyphthalimidines. By contrast, as is well known, reactions of the ring tautomeric acid chlorides

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corresponding to phthalaldehydic and *o*-benzoylbenzoic acids with amines lead to hydroxyphthalimidines.[8,9,11,12]

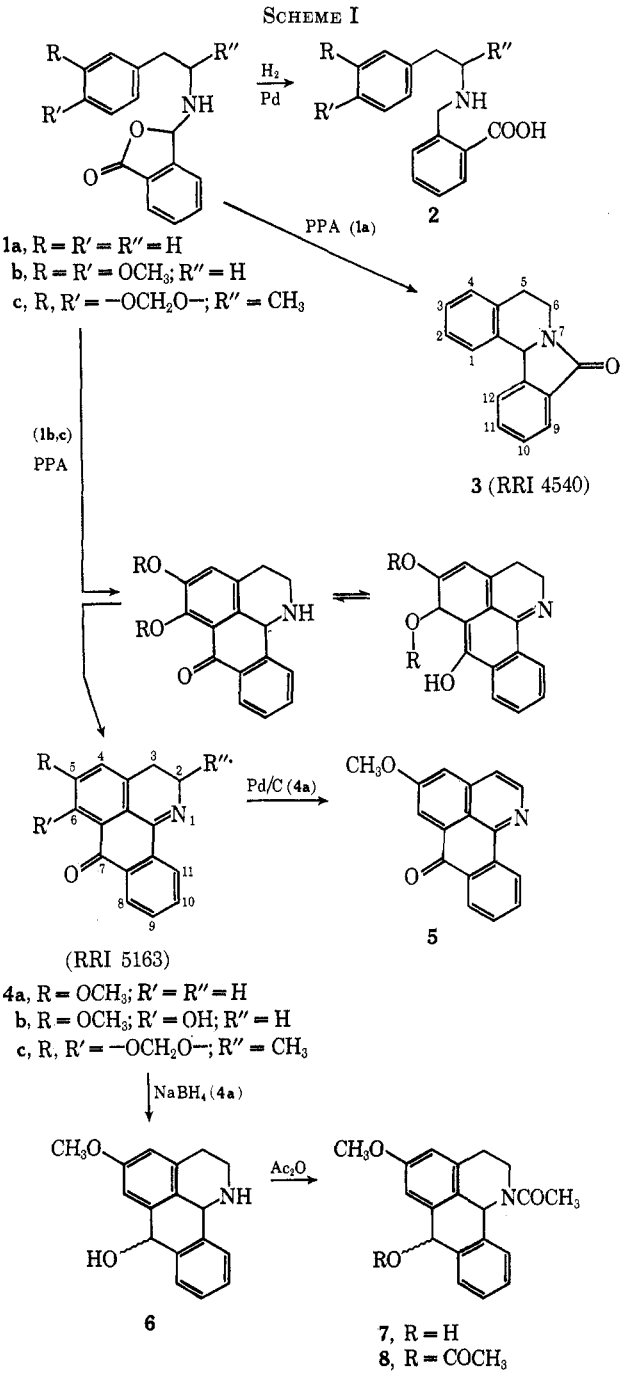
We found that polyphosphoric acid (PPA) cyclization at 100° of crude material consisting largely of **1a** gave a colorless lactam **3**, the same as that reported[8] as the product of H_2SO_4 cyclization of 3-hydroxy-*N*-(β-phenylethyl)phthalimidine. Similar cyclizations of **1b** and **c**, however, gave quite different results. The main product (yield *ca.* 30%) from **1b** was not a lactam but rather a basic, yellow (or orange) substance. Its analytically determined empirical formula was $C_{17}H_{13}NO_2$ (mol wt 263), although $FeCl_3$ tests, together with mass spectra, indicated the presence of a phenolic impurity, $C_{17}H_{13}NO_3$ (mol wt 279), as well as a trace of another substance, $C_{18}H_{15}NO_3$ (mol wt 293). As it was practically impossible to remove the (crypto)phenolic constituent completely by extraction with bases, the $C_{17}H_{13}NO_2$ compound was difficult to purify completely; nonetheless, good analyses were secured, and further work as follows established its structure as **4a**. Although basic (giving red solutions with acids), it did not react with dimethyl sulfate, iodomethane, or acetic anhydride except under drastic conditions. The uv spectrum closely resembled that of 2-methoxyanthraquinone. The nmr spectrum with six aromatic protons, one of them meta (but not ortho) coupled, and three methoxyl protons (δ 3.9), agreed with structure **4a**. The ir spectrum, lacking NH absorption, had a strong 6.05-μ peak, evidently conjugated C=O and/or C=N. The presence of both these unsaturated groups became apparent on $NaBH_4$ reduction, when the ir 6.05-μ peak disappeared, and a basic carbinol **6** was obtained. From this compound in turn by treatment with Ac_2O at 100° there was obtained hydroxy *N*-acetyl derivative **7**, and further Ac_2O reaction (reflux) gave the *O,N*-diacetyl derivative **8**. Finally, aromatization of **4a** to **5** with Pd/C under mild conditions (refluxing xylene) afforded evidence of a dihydroisoquinoline moiety in **4a**.

Thus it was evident that PPA cyclization of **1b** led, *via* two ring closures[7] and loss of the elements of methanol, mainly to **4a** and in part, by loss of the elements of methane, to a minor amount of phenolic congener, probably **4b**, and to very little **4** (R = R′ = OCH_3).

Similar cyclization of methylenedioxy compound **1c** gave **4c**, which however was rather unstable and formed in much lower yield than **4a**. Correct analysis and spectra (ir 6.03 μ; uv similar to that of **4a**; nmr consistent with **4c**; mass spectrum 291) having established structure **4c**, it was evident that a similar loss of 2 H without accompanying dealkoxylation had occurred. Phenolic substances were also present after this cyclization, but they were not amenable to isolation and characterization.

The course of these ring closures seems fairly clear, although certain questions remain unanswered. After cyclization of iminium acids corresponding to **1b,c** to tetrahydroisoquinolines, the reactivity of position 8 therein owing to the 7-alkoxy group is such that further carbonylium ion attack, very similar to that leading from 2-(*m*-methoxybenzoyl)benzoic acids to corresponding anthraquinones,[13] occurs, giving a 10-aminoanthrone relative. The driving force for dehydrogenation of such an intermediate to an anthraquinone imine very likely is in itself great and, as shown by the isolation of **4c**, is not necessarily related to loss of oxygen from the aromatic carbon ortho to the anthraquinone C=O. The loss of this oxygen, an unusual phenomenon, predominating in **1b** → **4a**, could proceed *via* first demethylation to chelated hydroxy ketone **4b** (a well-known type) and then loss of water, or it might involve direct loss of methanol. One tautomeric form of a possible intermediate, 5,6-dioxytetrahydro-7-dibenzo-[*de,h*]quinolone which might lose ROH directly, is indicated in Scheme I, although we do not necessarily claim its validity. In any event there is at least one

SCHEME I



5

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excellent analogy to our findings to be found in work with liriodenine analogs,[14] wherein from a partially hydrogenated azabenzanthrone (aporphinone) of a similar type there was eliminated in the course of work-up an *o*-methoxyl group situated (vinylogously) in respect to C=O so as to resemble a methyl enol ether, as in the present case.

Aromatic methoxyl loss is an unusual synthetic reaction, but the possibility may exist that it occurs in critical intermediates at appropriate oxidation levels in some biogenetic cyclizations leading to series of related alkaloids in which the number of oxy groups varies. In view of current interest in aporphines and other isoquinoline alkaloids,[15-18] the findings presented here may be of interest.

Experimental Section[19]

5,6,8,12b-Tetrahydro-8-isoindolo[1,2-*a*]isoquinolone (3).—The condensation product **1a** from 13.9 g (0.115 mol) of β-phenylethylamine and 17 g (0.113 mol) of phthaldehydic acid (200 ml of toluene, Dean–Stark trap, refluxed 1 hr, solvent evaporated; mp 156–158°, acid-soluble; ir 5.70–5.88 μ) and 250 g of PPA were heated 1 hr on a steam cone with stirring. Treatment with ice and water, extraction with ether, isolation of neutral product by evaporation of washed (dilute NaOH, dilute HCl, water) and dried ($MgSO_4$) ether solution, and recrystallization from ether gave 17 g (64%) of colorless crystals: mp 116–118° (lit.[8] mp 114–116°); ir 5.96 μ; uv 278 nm (ε 1840).

Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.58; H, 5.82; N, 5.92.

Reaction of **3** (20 g) with $LiAlH_4$ (40 g) in THF (250 ml; refluxed and stirred 10 hr) and work-up (150 ml of water, filtration, evaporation, residue separated into neutral and basic components) gave 3.4 g of the corresponding tetracyclic, tertiary amine, characterized as the hydrochloride, mp 221–225° dec (from ethanol–ether).

Anal. Calcd for $C_{16}H_{15}N \cdot HCl$: C, 74.55; H, 6.26; N, 5.34. Found: C, 74.82; H, 6.51; N, 5.35.

A neutral product (5.1 g) was also obtained from this $LiAlH_4$ reaction and assigned the structure **12b-hydroxy-5,6,8,12b-tetrahydro-8-isoindolo[1,2-*a*]isoquinolone**, colorless crystals from ethyl acetate: mp 200–203° dec; ir 3.06 and 5.99 μ; uv 248–254 nm (ε 4420) and inflections 264 (3860) and 272 (2950).

Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.47; H, 5.22; N, 5.57. Found: C, 76.35; H, 5.20; N, 5.51.

2,3-Dihydro-5-methoxy-7(7*H*)-dibenzo[*de,h*]quinolone (4a).—Condensation of 27 g (0.149 mol) of homoveratrylamine and 22.5 g (0.150 mol) of phthaldehydic acid in 300 ml of toluene or benzene, with or without 0.5–1.0 g of TSO_3H (1.5-hr reflux under water trap), gave a crude, acid-soluble, viscous oil, ir 5.68 μ (**1b**). This syrup and 425 g of PPA were heated 0.7 hr on a steam cone with stirring. The cooled material was treated with 1.5 l. of ice and water and stirred 1–2 hr. The deep red, aqueous solution was separated from dark, tarry residue by decantation and filtration and made basic by gradual addition (ice bath) of 20% NaOH solution. Crude, orange-brown crystals which separated were collected, washed with water, and dried, yield 13.5 g (34%). On trituration with methanol there was obtained 10.3 g (26%) of orange-yellow crystals: mp 163–166° dec; mass spectrum M 293 (very weak), 279 (*ca.* 6–10%), and 263 (90% or more). Recrystallization from ethanol or methanol gave **4a** as yellow crystals, mp *ca.* 170° dec, still somewhat contaminated with phenolic material although sufficiently pure for further reactions: mass spectrum M^+ 263 with *m/e* 236 (−HCN), 248 (−CH_3), and 219, as well as *m/e* 279 (relative intensity *ca.* 5%) and 262 (−OH). The 279 phenolic constituent was still present after treatment of the material with warm 21% NaOH solution.

The compound was relatively insoluble in EtOAc, acetone, and DMSO. It did not react with diazomethane, with iodomethane (DMF) or methyl sulfate, or with Ac_2O at 100°.

The crude cyclization product, before recrystallization or trituration with solvents, was found to consist of 15% of the phenolic compound, which was isolated and characterized as follows. Preparative tlc ($CHCl_3$ solution, on silica) with 0.65 g of crude, orange crystals gave (fraction 1) 110 mg (17%) of orange crystals: mp 163–167° dec; $R_f \simeq 2.5$; $FeCl_3$ test deep blue-green; mass spectrum M^+ 293:M^+ 279 (1:8 intensity ratio). Trituration and recrystallization of the sample from EtOAc gave orange needles (**4b**): mp 173.5–174.5° dec; ir 6.10–6.18 (rel weak, chelated) and 6.29 μ; uv 240, 278, 324, and 428–430 nm (log ε 4.53, 4.13, 3.82, and 3.71, respectively); M^+ 279.

Anal. Calcd for $C_{17}H_{13}NO_3$: C, 73.11; H, 4.69; N, 5.02. Found: C, 73.31; H, 4.82; N, 4.94.

Fraction 2 from tlc [529 mg (81%), mp 166–170° dec, $R_f \simeq 3.5$, $FeCl_3$ negative, M^+ 263] was essentially pure **4a**. Recrystallization from methanol gave yellow crystals: mp 168–170° dec; ir 6.05 and 6.28 μ; uv 226, 248–252, 259, 275, 316, 364, and 380 nm (log ε 4.43, 4.34, 4.37, 4.26, 3.68, 3.57, and 3.62, respectively); nmr ($CDCl_3$) δ 8.5–7.5 (m, 5, aromatic protons at positions 6, 8, 9, 10, and 11), 6.95 (m, 1, $J \leq 3$ Hz, meta-coupled 4-proton), 4.13 (t, 2, $J = 7$ Hz, 3-methylene), 3.9 (s, 3, OCH_3), and 2.85 (t, 2, $J = 7$ Hz, 2-methylene).

Anal. Calcd for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.42; H, 4.97; N, 5.22.

Fraction 3 from tlc [16 mg (2.5%), mp *ca.* 165–170°, $R_f \simeq 5.5$, $FeCl_3$ negative], had mass spectral peaks at 261 and 231 (intensity ratio 2:1), presumably representing monomethoxy (**5**) and deoxy aromatized compounds, respectively.

2,3-Dihydro-2-methyl-5,6-methylenedioxy-7(7*H*)-dibenzo[*de,h*]quinolone (4c).—Similar cyclization of 15 g of the crude condensation product (benzene) of phthalaldehydic acid and β-(3,4-methylenedioxyphenyl)isopropylamine (ir 5.68–5.72 μ) with 150 g of PPA at 100° for 20 min was accompanied by decomposition (dark brown, foaming). After hydrolysis with 1 l. of ice and water, the clarified, red solution was neutralized with NaOH. From the deep green solution there was slowly deposited (3 days, 0°) *ca.* 0.5 g of crystalline material, which was collected, washed with water, dried, and recrystallized from ethyl acetate, light orange crystals, tending to become greenish in air especially in the presence of solvents: mp 214–217° dec; ir 6.03 μ; uv 233 nm (ε 35,030), 405 (5480), and a series of inflections at 251 (21,540), 272 (16,270), and 319 (5750); nmr ($CDCl_3$) δ 8.4–8.2 (m, 2, protons 8 and 11), 7.8–7.5 (m, 2, protons 9 and 10), 6.9 (s, 1, 4-proton), 6.25 (s, 2, OCH_2O), 4.0 (m, 1, 2-methine), 3.2–2.5 (m, 2, 3-methylene), and 1.63 (d, 3, CH_3); mass spectrum M^+ 291 with peaks 276 (−CH_3), 263 (−CO), 264 (−HCN), 248 (−CO, −CH_3).

Anal. Calcd for $C_{18}H_{13}NO_3$: C, 74.21; H, 4.50; N, 4.81. Found: C, 73.97; H, 4.75; N, 4.75.

***o*-[β-(3,4-Dimethoxyphenylethyl)aminomethyl]benzoic Acid (2b).**—Hydrogenation (40 psi) of 8.7 g of crude **1b** in EtOAc (150 ml) in the presence of 5 g of 10% Pd/C at 50° for 2 hr afforded crystals: mp 165.5–167° dec (from ethanol); water soluble; ir broad aminium and carboxylate (6.12 μ) bands; uv 226 nm (ε 13,580) and 277 (3640).

Anal. Calcd for $C_{18}H_{21}O_4N$: C, 68.55; H, 6.71; N, 4.44. Found: C, 68.26; H, 6.80; N, 4.67.

Compound 2c, similarly prepared from **1c**, had comparable properties, crystals from ethanol, mp 172.5–173.5° dec.

Anal. Calcd for $C_{18}H_{19}NO_4$: C, 68.99; H, 6.11; N, 4.47. Found: C, 68.64; H, 6.31; N, 4.40.

5-Methoxy-7(7*H*)-dibenzo[*de,h*]quinolone (5).—Compound **4a** (1.5 g) in xylene (250 ml) with 10% Pd/C catalyst (1.3 g) was refluxed 1 hr, and the suspension was filtered while hot. Evaporation of the solvent gave (quantitatively) crystalline residue. Recrystallization from ethyl acetate afforded golden yellow crystals: mp 180–181°; ir 6.03 μ and doublet 6.18–6.25 μ; uv 247, 311, and 382 nm (log ε 4.70, 3.72, and 3.99, respectively) with inflections at 275 (3.81), 302 (3.69), and 394 (3.99); nmr ($CDCl_3$) δ 8.8–7.1 (m, 8, aromatic protons, with one meta-

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(19) Melting points were obtained using Thomas-Hoover silicone oil bath; uv curves (MeOH solutions) were measured with a Cary 14 recording spectrophotometer; ir spectra (Nujol mulls) were taken on a Perkin-Elmer 21 double-beam instrument; mass spectra were recorded using a MS-902 double-focusing apparatus. We are indebted to Miss Ruth Behnke for nmr spectra (Varian A-60; TMS internal standard) and interpretation thereof, as well as to Mr. George Robertson, Mr. Rudolf Oeckinghaus, Dr. Reginald Puckett, Miss Barbara Biffar, Miss Natalie Cahoon, Mr. Charles Navarro, Mr. Anis Hamden, and Mr. Mike Hotolski of the staff of Mr. Louis Dorfman for microanalytical and spectral data, and to Mr. B. Korzun for chromatographic work.

coupled 6-proton discernible *ca.* δ 8.04; J = 2.5 Hz), 3.92 (s, 3, OCH_3); mass spectrum M^+ 261 with 231 ($-OCH_3$), 203 ($-CO$), and M^+ 277 (low intensity).

Anal. Calcd for $C_{17}H_{11}NO_2$: C, 78.15; H, 4.24; N, 5.36. Found: C, 77.91; H, 4.36; N, 5.47.

5-Methoxy-7-hydroxy-1,2,3,11b-tetrahydro-7*H*-dibenzo[*de*,*h*]-quinoline (6).—Treatment of a suspension of **4a** in methanol with an excess (4–5 parts by weight) of $NaBH_4$ resulted in effervescence and solution of the material. After heating on a steam cone 20 min while evaporating most of the methanol, the cooled residue was treated with water. The collected, washed (water), and dried product, on recrystallization from methanol, gave colorless crystals: mp 191–193°; ir 6.18 μ (weak) together with bonded OH and NH bands; uv 276 nm (ϵ 1960) and 284 (2010).

Anal. Calcd for $C_{17}N_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.65; H, 6.58; N, 5.28.

The compound gave temporary, intense blue (or red) colors with strong acids.

***N*-Acetyl derivative 7** was obtained by warming a sample of the basic carbinol **6** with excess acetic anhydride at 100° for 1.5 hr. The solution was evaporated and the residue recrystallized from ethyl acetate, giving colorless crystals: mp 225–227°; ir 2.92 and 6.14 μ; uv 276 nm (ϵ 1810) and 283 (1870); nmr (DMSO) δ 7.83–6.6 (m, 6, aromatic protons), 6.36 (d, 1, D_2O exchange, OH), 5.9–5.4 (m, 2, benzhydryl protons), 3.74 (s, 3, OCH_3), 3.1–2.6 (m, 4, methylene protons), and 2.33–2.07 (complex s, 3, $NHCOCH_3$).

Anal. Calcd for $C_{19}H_{19}NO_3$: C, 73.76; H, 6.19; N, 4.53. Found: C, 73.84; H, 6.25; N, 4.38.

***O*,*N*-Diacetyl derivative 8** was obtained by refluxing **6** or **7** (1 g) with acetic anhydride (45 ml) for 4 hr. Evaporation, trituration of the brown-yellow residue with ether–ethyl acetate, and recrystallization from methanol gave slightly yellowish crystals: mp 188–190°; ir 5.71 and 6.07 μ; uv 278–279 nm (ϵ 1900); nmr ($CDCl_3$) δ 7.4–6.55 (m, 6, aromatic protons), 6.08 (broad s, 1, 7-proton), 5.43 (s, 1, 11b-proton), 3.8 (s, 3, OCH_3), 3.1–2.7 (m, 4, methylene protons), and 2.5–2.17 (m, 6, $COCH_3$; complexity of the latter signals indicating more than one isomer and/or slight contamination with a phenol acetate).

Anal. Calcd for $C_{21}H_{21}NO_4$: C, 71.78; H, 6.02; N, 3.99. Found: C, 71.76; H, 6.12; N, 3.93.

Hydrogenation of **7** or **8** in glacial HOAc in the presence of 10% Pd/C at 60–70° (3 hr) apparently led to hydrogenolysis of both benzhydryl (9,10-dihydroanthracene) groups and also to reduction of one of the aromatic rings, *i.e.*, to a crystalline **2-methoxy-4-(β-acetylaminoethyl)octahydroanthracene**, crystals from ether: mp 147–148°; ir 3.04, 6.12, and 6.45 μ; uv 274 nm (ϵ 1510) and 283 (1690).

Anal. Calcd for $C_{19}H_{27}NO_2$: C, 75.71; H, 9.03; N, 4.65. Found: C, 75.76; H, 9.06; N, 4.58.

Registry No.—**2b**, 28399-68-0; **2c**, 28455-52-9; **3**, 17416-64-7; **3** HCl, 28399-70-4; **4a**, 28399-71-5; **4b**, 28399-72-6; **4c**, 28399-73-7; **5**, 28399-74-8; **6**, 28399-75-9; **7**, 28399-76-0; **8**, 28399-77-1; 12b-hydroxy-5,6,8,-12b-tetrahydro-8-isoindolo[1,2-*a*]isoquinolone, 28455-53-0; 2-methoxy-4-(β-acetylaminoethyl)ctahydroanthracene, 28390-69-4.

Polycyclic Orthoquinonoidal Heterocycles. Thieno[3,4-*b*]quinoline and Naphtho[2,3-*c*]thiophene

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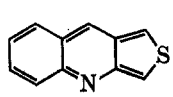
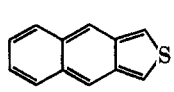
The formation of transient thieno[3,4-*b*]quinoline (**1**) and naphtho[2,3-*c*]thiophene (**2**) has been demonstrated in the synthesis of the exo NPMI adduct of **1** and a mixture of the exo and endo NPMI adducts of **2**. These adducts were isolated and characterized. Attempts to prepare **1** by the dehydration of 1,3-dihydrothieno[3,4-*b*]-quinoline 2-oxide (**8**) and dehydrogenation of 1,3-dihydrothieno[3,4-*b*]quinoline (**7**) were unsuccessful as were attempts to prepare **2** *via* the analogous dehydration of 1,3-dihydronaphtho[2,3-*c*]thiophene 2-oxide (**10**). The stabilities of **1** and **2** are discussed relative to one another and with regard to systems incorporating similar structural features.

This paper describes the attempted synthesis of thieno[3,4-*b*]quinoline (**1**) and naphtho[2,3-*c*]thiophene (**2**) from their precursor sulfoxides, 1,3-dihydrothieno-



1

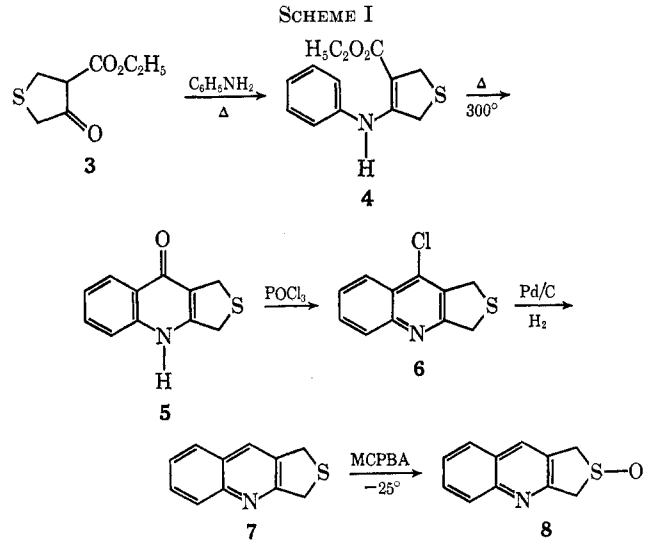


2

[3,4-*b*]quinoline 2-oxide (**8**) and 1,3-dihydronaphtho-[2,3-*c*]thiophene 2-oxide (**10**), or their precursor sulfides, 1,3-dihydrothieno[3,4-*b*]quinoline (**7**) and 1,3-dihydronaphtho[2,3-*c*]thiophene (**9**), in order to ascertain their relative stabilities compared to naphtho[1,2-*c*]thiophene.[2]

Synthesis of 1,3-Dihydrothieno[3,4-*b*]quinoline 2-Oxide (8).—The synthesis of **8** was accomplished as outlined in Scheme I. Reaction of aniline and ethyl 3-ketotetrahydrothiophene-4-carboxylate (**3**) following the procedure of Brown, *et al.*,[3] gave ethyl 3-anilino-2,5-dihydrothiophene-4-carboxylate (**4**) in 78% yield.

Scheme I



The occurrence of the imino tautomer of **4** was excluded by the presence of a sharp N–H stretching band at 3200 cm^{-1} in its infrared spectrum. Thermal ring closure to 4*H*-1,3,4,9-tetrahydrothieno[3,4-*b*]-quino-

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(2) M. P. Cava and N. M. Pollack, *J. Amer. Chem. Soc.*, **88**, 4112 (1966).

(3) R. J. Brown, F. W. S. Carver, and B. L. Hollingsworth, *J. Chem. Soc.*, 2624 (1962).