6.12, 6.25, 6.35 μ; nmr 429–463.5 (m), 382 (s), 304 (q, J = 6.5 cps), 93 (d, J = 6.5 cps), 48 cps (s).

Anal. Calcd for $C_{27}H_{32}N_2$: C, 84.33; H, 8.39; N, 7.29. Found: C, 84.60; H, 8.30; N, 7.68.

Crystallization of **5** from ether–hexane gave 0.66 g of a yellow crystalline product: mp 156–160°; $[\alpha]^{26}D$ +26° (*c* 1, $CHCl_3$); λ_{max}^{MeOH} 259–261 mμ (ε 16,750); λ_{min} 234.5–235.5 mμ (ε 8725); λ_{max}^{KBr} 3.25, 6.15, 6.22 μ; nmr 446 (s), 442 (s), 373 (s), 303 (q, J = 7 cps), 93 (d, J = 7 cps), 45 cps (s).

Anal. Calcd for $C_{27}H_{32}N_2$: C, 84.33; H, 8.39; N, 7.29. Found: C, 84.52; H, 8.30; N, 7.32.

19-Nor-2′-phenyl-1(10)-2,4,17(20)-pregnatetraeno[3,2-*c*]pyrazole (9).—To a warm solution of 0.48 g of 19-nor-2′-phenyl-2,4,17(20)-pregnatrieno[3,2-*c*]pyrazole (**5**) in 40 ml of acetone was added portionwise with stirring over a period of 1 hr 0.35 g of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone. The reaction mixture, which contained a crystalline product, was allowed to stand at room temperature for an additional hour. Then the colorless, crystalline product was collected, washed with acetone, and dried, yield 0.27 g, mp 198.5–200.5°. The combined filtrate and washings were concentrated to 25 ml. On standing at room temperature for 15 hr, the resultant mixture afforded an additional 0.04 g of **9**, mp 196.5–201.5°. Crystallization of the first crop from acetone raised the mp to 201.5–204.5°; $[\alpha]^{26}D$ +15° (*c* 1, $CHCl_3$); $\lambda_{max}^{CHCl_3-MeOH}$ 256.6 mμ (ε 28,450), 306 (7900); λ_{min} 232.5–233.5 mμ (ε 8860), 283.5–286 (5175); λ_{max}^{KBr} 3.27, 6.12, 6.13 μ; nmr 485.5 (s), 442.5–461 (m), 307 (q, J = 7 cps), 180 (t, J = 5 cps), 95 (d, J = 6.5 cps), 47.5 cps (s).

Anal. Calcd for $C_{27}H_{30}N_2$: C, 84.77; H, 7.91; N, 7.32. Found: C, 84.70; H, 7.82; N, 7.61.

19-Nor-1′-phenyl-4,6,17(20)-pregnatrieno[3,2-*c*]pyrazole (10).—To a warm solution of 1.01 g of 19-nor-1′-phenyl-4,17(20)-pregnadieno[3,2-*c*]pyrazole (**4**) in 30 ml of acetone was added portionwise with stirring over a period of 1 hr 0.78 g of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone. The reaction mixture was allowed to stand at room temperature for 16 hr and then treated with a dilute solution of sodium sulfite. The reaction mixture was concentrated. The residue was diluted with ice water. The resultant brown solid was collected, washed with water, and dried. It was chromatographed on 100 g of neutral alumina. Elution of the column with 30% hexane in benzene gave 0.33 g of a pale yellow crystalline product, mp 183–186°. Crystallization from acetone gave **10** as colorless crystals, mp 187.5–190°. Admixed with **9**, it melted at 168–177°; $[\alpha]^{26}D$ −514° (*c* 0.25, $CHCl_3$); $\lambda_{max}^{CHCl_3-MeOH}$ 246.5–248.5 mμ (ε 9030), 320–321 (37,700); λ_{min} 237.5–239 mμ (ε 8500), 271–273 (5550); λ_{max}^{KBr} 3.28, 6.24, 6.38 μ; nmr 435.5–453.5 (m), 377 (d, J = 10 cps), 351 (d, J = 10 cps), 303.5 (*q*, J = 65 cps), 184 (d, J = 7 cps), 93 (d, J = 6.5 cps), 47.5 cps (s).

Anal. Calcd for $C_{27}H_{30}N_2$: C, 84.77; H, 7.91; N, 7.32. Found: C, 85.03; H, 7.99; N, 7.45.

Ultraviolet Absorption Maxima and Minima of 3-Methyl-1-phenylindazole (6):[4a,6] λ_{max}^{MeOH} 251 mμ (ε 34,050), 304–307 (13,500); λ_{min} 229–231 mμ (ε 8400), 278 (5080).

Ultraviolet Absorption Maxima and Minima of 2-Phenylindazole (7).—This substance was prepared according to the procedure of Krbechek and Takimoto;[4b] λ_{max}^{MeOH} 235–236 mμ (ε 21,700), 294–295 (15,800), λ_{min} 257 mμ (ε 2290).

Registry No.—**4**, 28504-58-7; **5**, 28504-59-8; **6**, 1575-29-7; **7**, 3682-71-1; **9**, 28504-62-3; **10**, 28504-63-4.

Synthesis of 1,10,11,11a-Tetrahydro-11a-methyl-2*H*-naphth[1,2-*g*]indol-7-ol, an Equilenin-Like 15-Aza Steroid[1]

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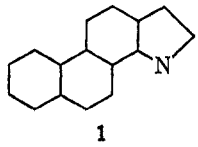
Received November 23, 1970

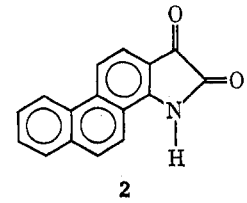
This study reports the synthesis and characterization of the 15-azaequilenin derivative 1,10,11,11a-tetrahydro-11a-methyl-2*H*-naphth[1,2-*g*]indol-7-ol (**6a**) as well as the methyl ether **6b** of the above compound and the novel model compound 3,3a,4,5-tetrahydro-3a-methyl-2*H*-benz[*g*]indole (**7**).

Steroids which have nitrogen incorporated in the cyclopentaphenanthrene nucleus have been shown to possess a wide range of physiological activities.[3–5] Interestingly, naph[1,2-*g*]indoles or 15-aza steroids of general formula **1** represent an almost totally neglected area of organic synthesis despite the fact that these compounds combine the steroid and indole nuclei in a single structure and may be expected to demonstrate significant biological activity.



1

A literature search revealed only four examples of 15-monoaza steroid structures. Naphthisatin **2** was synthesized in the 1930's as a "synthetic decarboxylase,"[6] and compounds **3–5** were intermediates in steroid–terpene structure correlations.[7] No pharmacological data on the aforementioned compounds are available.



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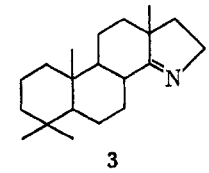

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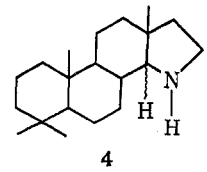

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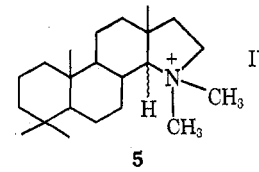


5

(1) We gratefully acknowledge support of this work by a grant to the Oklahoma State University from the American Cancer Society, Grant IN-91A. Presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971. We thank the Merck Sharp and Dohme Co. for partial support.

(2) (a) Department of Chemistry; NDEA Fellow, 1966–1969; this work is abstracted in part from the thesis submitted in partial fulfillment of the Doctor of Philosophy degree in the Oklahoma State University. (b) Department of Microbiology.

(3) M. Alauddin and M. Martin-Smith, *J. Pharm. Pharmacol.*, **14**, 325 (1962).

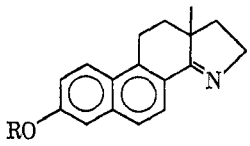
(4) M. Martin-Smith and F. Sugrue, *ibid.*, **16**, 568 (1964).

(5) H. Singh, S. Padmanabhan, and V. Parashar, *J. Proc. Inst. Chem., Calcutta*, **39**, 54 (1967).

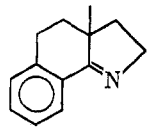
(6) W. Langenbeck and K. Weissenborn, *Ber.*, **72** (B), 724 (1939).

(7) M. Fetizon and M. Golfier, *Bull. Soc. Chim. Fr.*, 870 (1966).

This study reports the complete synthesis and characterization of the 15-azaequilenin derivative, 1,10,11,-11a-tetrahydro-11a-methyl-2*H*-naphth[1,2-*g*]indol-7-ol (**6a**), as well as the unique benzindole **7** produced in model-system studies.

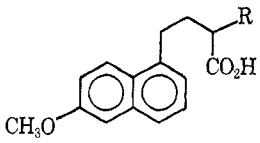


6a, R = H
b, R = OCH_3

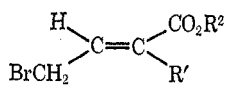


7

The synthesis of **6a** requires the naphthalenebutyric acid **8a**, previously prepared by a variety of laborious multistep processes.[8-10] In this study the general



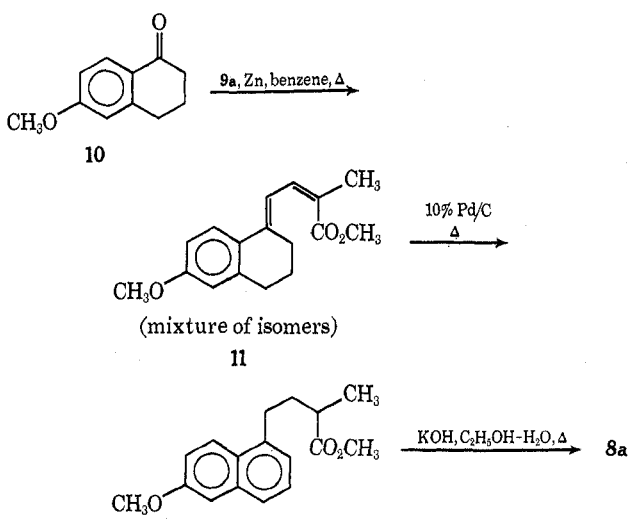
8a, R = CH_3
b, R = H



9a, R′ = R^2 = CH_3
b, R′ = H; R^2 = C_2H_5

method of Stork[11] was applied to the synthesis of **8a** but using the bromotiglate **9a** rather than the bromocrotonate **9b** employed by Stork (Scheme I). Actually,

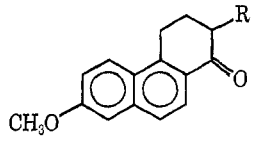
SCHEME I



the diene ester **11** was distilled but it undoubtedly was a mixture of isomers.

The bromo ester **9a**, prepared by the method of Inhoffen and coworkers,[12] could only be isolated in a crude state (see Experimental Section). Crude **9a**, however, proved satisfactory for use in the synthesis of **8a**.

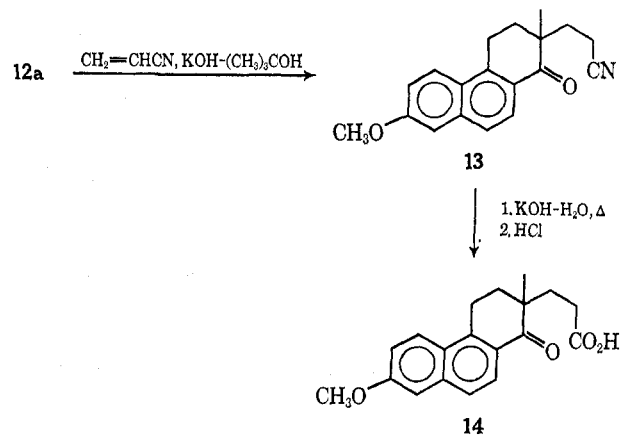
Acid **8a** was then cyclized with polyphosphoric acid[13] to yield the known phenanthrone **12a**.[8-10] This cyclization, which can be performed in 30 min in an open beaker, produces **12a** in 86% yield and is thus superior in terms of ease and convenience to any published method for the conversion of **8a** to **12a**. Ketone **12a**



12a, R = CH_3
b, R = H

was condensed with acrylonitrile in *tert*-butyl alcohol in the presence of aqueous KOH (this general method is recorded[14,15]). The resulting nitrile, **13** (not isolated), upon hydrolysis provided the novel and previously unknown phenanthrenepropionic acid **14** (Scheme II) in a yield of 56.5% (based on **12a**). This

SCHEME II



yield was determined from the weighed compound obtained after one chromatogram and two recrystallizations.

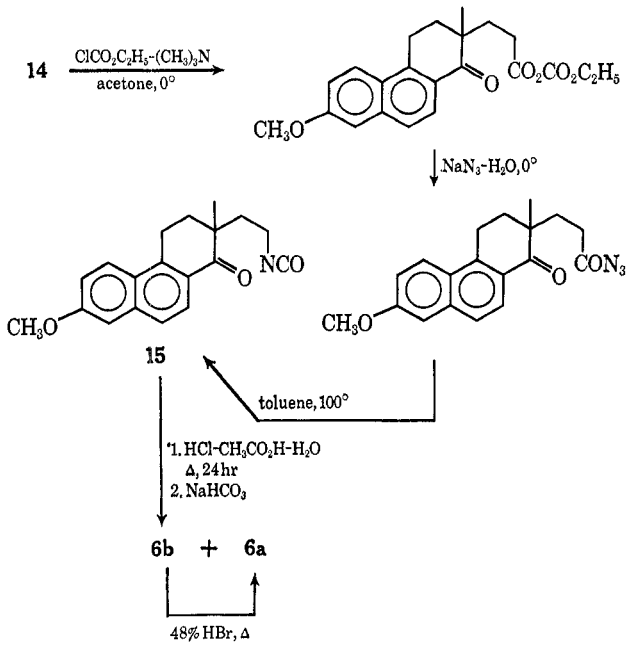
Acid **14** was subjected to the modified Curtius rearrangement procedure of Weinstock[16] as adapted by Fetizon and Golfier.[7] The resulting steroidal imine ether **6b** was then hydrolyzed with boiling 48% HBr to the title compound **6a**. Some **6a** was, in fact, produced directly during the hydrolysis of isocyanate **15**, especially if prolonged heating was employed (Scheme III).

The α-methylation of 1-tetralone was examined as a model system for the preparation of **12a** from the unsubstituted phenanthrone **12b** (compound **12b** being conveniently available from **8b**).[11] 2-Methyl-1-tetralone (**16**) was successfully produced in high yield from 1-tetralone by application of the methods of Ireland and Marshall,[17] *i.e.*, reductive desulfurization of the 2-*n*-butylthiomethylene derivative of a ketone. Unfortunately, **12a** could not be realized in satisfactory condition by the foregoing approach, since a complicated mixture was obtained in the reduction step.

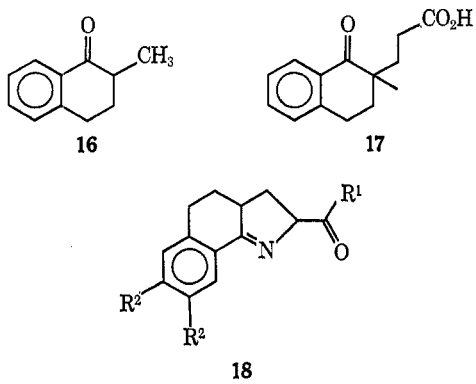
Compound **16** was subjected, in a pilot study, to the same series of reactions eventually used with phenanthrone **12a**. The synthesis of the resulting novel 3,3a,4,5-tetrahydro-3a-methyl-2*H*-benz[*g*]indole (**7**)

(8) W. Bachmann, S. Kushner, and A. Stevenson, *J. Amer. Chem. Soc.*, **64**, 979 (1942).
(9) G. Haberland and E. Blanke, *Ber.*, **70**, 169 (1937).
(10) A. Wilds and W. Close, *J. Amer. Chem. Soc.*, **69**, 3079 (1947).
(11) G. Stork, *ibid.*, **69**, 2936 (1947).
(12) H. Inhoffen, S. Bork, and U. Schweiter, *Justus Liebigs Ann. Chem.*, **880**, 1 (1953).
(13) F. Snyder and F. Werber, "Organic Syntheses," Collect. Vol. III, E. Horning, Ed., Wiley, New York, N. Y., 1963, p 798.
(14) R. Frank and F. Pierle, *J. Amer. Chem. Soc.*, **73**, 724 (1951).
(15) M. Robinson, *Tetrahedron*, **1**, 49 (1957).
(16) J. Weinstock, *J. Org. Chem.*, **26**, 3511 (1961).
(17) R. Ireland and J. Marshall, *ibid.*, **27**, 1616 (1962).

SCHEME III



represents only the second time that the production of this type of compound has been recorded. Several members of the general formula **18** were reported to be "adrenolytic central nervous system depressants and analgetic agents."[18] The hydrochloride of **18** (R^1 = OH; R^2 = H) has been prepared by the acid hydrolysis of the condensation product of *N,N,N*-trimethyl-1,2,3,4-tetrahydro-1-oxo-2-naphthalenemethylammonium chloride and diethyl acetamidosodiomalonate.[18]



Aza steroids **6a** and **6b** have been subjected to a program of testing and produced cell lysis in *Bacillus subtilis* and inhibited the growth of a species of *Flavobacterium, Escherichia coli,* and *Pseudomonas fluorescens.* The results of this biological survey will be reported in detail elsewhere.

Experimental Section[19]

Preparation of 6-Methoxy-α-methyl-1-naphthalenebutyric Acid (8a).[11]—A zinc strip (0.01 in. thick, 270 g, 4.1 g-atoms) was cut into approximately 0.25 by 0.5 in. pieces and washed consecutively with dilute HCl, distilled H_2O, acetone, and anhydrous ether. The zinc was then dried at 100° in an oven for about 0.5 hr before use.

The zinc, 700 ml of anhydrous, reagent-grade benzene, and 18.0 g of anhydrous $HgCl_2$ were placed in a 5-l. flask equipped with a condenser and N_2 inlet. This mixture was stirred under N_2 purge for 0.5 hr. Bromo ester **9a**[20] (260 g, 1.34 mol) and 6-methoxy-1-tetralone (**10**) [260 g, 1.48 mol (Aldrich Chemical Co.), mp 76–78° (lit.[11] mp 78.4–79°)] in 700 ml of ether and 300 ml of benzene, along with a crystal of iodine, were added at one time to the reaction flask. An exothermic reaction ensued accompanied by vigorous boiling of the solvent. At 1.5-hr intervals, 140 g (215 g-atoms) of zinc, 87 g (0.45 mol) of **9a**, and a crystal of iodine were added. This procedure was performed three times, the mixture being boiled and stirred under N_2 during the whole period.

Heating and stirring were continued for 3 hr after the last addition; the mixture was then cooled, poured into ice water, neutralized with acetic acid, and extracted with ether. The organic phase was extracted three times with 5% aqueous NH_4OH, once with H_2O, and once with saturated aqueous NaCl, and the resulting solution was dried ($MgSO_4$). After being filtered, the solution was evaporated on an aspirator and the residual oil was distilled *in vacuo*. A forerun consisting of unreacted **10** distilled at 110–150° (0.06 mm). The product amounted to 145 g (35.6% based on **10**) of crude methyl 4-(6-methoxy-1,2,3,4-tetrahydro-1-naphthylidene)tiglate (**11**), bp 180–200° (0.25 mm). This material is a viscous yellow oil which partially solidifies upon standing overnight.

The 145 g of **11** was heated to 250° with 23 g of 10% Pd/C for 6 hr under a CO_2 atmosphere. The mixture was then cooled, diluted with ether, filtered, and evaporated. The residue was heated at reflux for 12 hr with 50 g of KOH in 500 ml of 50:50 ethanol–H_2O. The resulting hydrolysate was diluted (H_2O), extracted three times with ether, and acidified (dilute HCl). The precipitate was filtered, washed well (H_2O), and vacuum dried to yield 120 g of dark solid. This solid was extracted with three 1.5-l. portions of boiling hexane, leaving behind a black undefined tar. On cooling, the hexane solution deposited 60 g of yellow-white crystals, mp 77–82°. Concentration of the mother liquor produced an additional 30 g of very crude **8a**. Total yield of **8a** was 90 g (24% based on **10**). An analytical sample of **8a** was crystallized from hexane: mp 85–86°, sealed tube (st) under vacuum (lit.[9] mp 86–87°); ν_{max}^{KBr} 1685 cm^{-1} (C=O); nmr (15% in $DCCl_3$) 1.26 (d, 3 H, CH_3), 1.67–3.27 (m, 5 H, CH_2 and CH), 3.82 (s, 3 H, OCH_3), 6.98–8.05 (m, 6 H, aromatic H), and 11.5 (s, 1 H, CO_2H).

Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.33; H, 7.07.

Preparation of 3,4-Dihydro-7-methoxy-2-methyl-1(2*H*)-phenanthrone (12a).[13]—Polyphosphoric acid (250 g of 115% PPA) was heated to 90° in a 600-ml beaker. Compound **12a** (60 g, 0.23 mol) was added and the mixture was stirred for 15 min. An additional 250 g of PPA was added and the mixture was reheated to 100° and then allowed to cool with stirring to 60°.

The resulting dark-brown syrup was poured into ice water and the yellowish solid which separated was filtered, washed well with distilled H_2O, and air-dried to yield 50.5 g of crude **12a**. This crude phenanthrone was dissolved in 350 ml of benzene, and the resulting solution was passed through 50 g (15 × 1 cm column) of alumina (Merck active aluminum oxide, neutral). The column was washed with additional benzene until no further material was eluted. Evaporation of the benzene *in vacuo* yielded 47.7 g (86%) of **12a** as a light yellow powder (mp 104.5–107.5°) suitable for use in the next step.

A 6-g sample of the above material was recrystallized three times from 50-ml portions of 1-butanol to yield an almost white, analytical sample (2.6 g) of **12a**: mp 107–108.5°, st, under vacuum (lit.[10] mp 109–110°); ν_{max}^{KBr} 1660 cm^{-1} (C=O); nmr (10% in $DCCl_3$) 1.29 (d, 3 H, CH_3), 1.56–3.44 (m, 5 H, CH_2 and CH), 3.89 (s, 3 H, OCH_3), and 7.05–8.18 (m, 5 H, aromatic H).

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.83; H, 6.60.

(18) N. Gruenfeld, U. S. Patent 3,232,953 (Feb 1, 1966); *Chem. Abstr.*, **64**, 12646 (1966).

(19) Nmr spectra were obtained on a Varian A-60 unit with tetramethylsilane (TMS = 0) as internal reference. Molecular weights by mass spectral analysis were performed on an LKB-9000 prototype unit. (We thank the NSF, Grant 6B-7731, for funds given to the Biochemistry Department for the mass spectrometer.)

(20) Methyl γ-bromotiglate (**9a**) was synthesized by the method of Inhoffen and coworkers.[12] Glpc and nmr analysis of the product indicated the presence of several isomers (probably methyl γ-bromoangelate and products derived by bromination of the allylic α-methyl group). Nevertheless, this bromo ester mixture proved satisfactory for use in the above procedure.

Preparation of 1,2,3,4-Tetrahydro-7-methoxy-2-methyl-1-oxo-2-phenanthrenepropionic Acid (14).[14,15]—The phenanthrone **12a** (2.80 g, 0.0182 mol) was placed in a 250-ml round-bottom, flask (fitted with an addition funnel and a N_2 inlet) and was dissolved in 100 ml of warm (60°) *tert*-butyl alcohol containing 0.2 g of aqueous 40% KOH. The ketone was only sparingly soluble in the alcohol and the reaction mixture had to be maintained at around 60° to effect solution, even though the literature[18] recommends that the temperature be kept below 40°.

Acrylonitrile [0.62 g, 0.0182 mol (Matheson, practical, grade, bp 75–78°)], dissolved in 10 ml of *tert*-butyl alcohol, was added dropwise over a 30-min period. The reaction mixture was stirred overnight at 60° under N_2. The solvent was then removed by aspirator, and the residue was boiled 36 hr with 50 ml of aqueous 20% KOH.

The reaction mixture was then diluted (H_2O), extracted two times (ether), and neutralized (dilute HCl). The resulting precipitate was washed with H_2O and air-dried to yield 3.3 g of dark-brown solid. This material was washed through a 10 × 1 silica gel (35 g) column with hot benzene and recrystallized twice from 150 ml of benzene to yield 2.0 g (56.5%) of white, crystalline **14**: mp 157.5–159°); ν_{max}^{KBr} 1680 (acid C=O) and 1655 cm^{-1} (ketone C=O); nmr (10% in $DCCl_3$) 1.22 (s, 3 H, CH_3), 1.76–2.67 (m, 6 H, aliphatic CH_2), 3.13–3.47 (bt, 2 H, benzylic CH_2), 3.90 (s, 3 H, OCH_3), 7.00–8.20 (m, 5 H, aromatic H), and 11.41 (s, 1 H, CO_2H).

Anal. Calcd for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 73.20; H, 6.31.

The above procedure was performed successfully on ten times the above scale. When the condensation was attempted in 1,4-dioxane using Triton B as a catalyst,[21] the yield of **14** was only 49% and phenanthrone **12a** was recovered unchanged in the amount of 32%.

Preparation of 1,10,11,11a-Tetrahydro-7-methoxy-11a-methyl-2*H*-naphth[1,2-*g*]indole (6b) and 1,10,11,11a-Tetrahydro-11a-methyl-2*H*-naphth[1,2-*g*]indol-7-ol (6a).[7,16]—The phenanthrenepropionic acid **14** (23 g, 0.076 mol, mp 155–157.5°) was dissolved in 500 ml of anhydrous, reagent grade acetone in a 1-l., three-necked, round-bottom flask equipped with a thermometer, N_2 inlet, and addition funnel with $CaSO_4$ drying tube. The mixture was cooled to −5° in a salt–ice bath, and 12.2 g (0.122 mol) of triethylamine was added dropwise, the temperature being kept below 0°. Ethyl chloroformate (4.7 g, 0.122 mol, Eastman) was then added with the temperature at 0°.

The mixture was stirred in the cold for 30 min and 10.3 g (0.16 mol) of NaN_3 in 40 ml of H_2O was added dropwise, again at 0°. The mixture was stirred at 0° for 1 hr and poured into ice water.

The crystalline azide that separated amounted to 18.0 g and decomposed with partial melting at 90–100° (st, under vacuum). The azide was dissolved in 500 ml of toluene and heated on a steam bath until gas evolution ceased (1–2 hr). Toluene was removed *in vacuo;* the residue amounted to 16.0 g of the crude isocyanate **15**. Crude **15** was boiled for 24 hr with 300 ml of 1:1:1 H_2O–glacial acetic acid–concentrated HCl. The mixture was cooled, diluted (H_2O), extracted three times (ether), filtered, and then neutralized (aqueous 10% $NaHCO_3$).

The resulting yellow solid (9.0 g), which had a very broad melting range (120–220°), was warmed (50–60°) with 150 ml of benzene, and the mixture was filtered. The residue was again extracted with an additional 150 ml of benzene. The filtrates were combined and reduced to 150-ml total volume by boiling on a hot plate. Cooling the solution to room temperature caused it to deposit a small additional quantity of material. This solution was then filtered and the benzene-insoluble residues (crude **6a**) were combined and set aside.

The yellow benzene solution was passed over a 15 × 1 cm column of neutral alumina (~50 g) and the column was washed with additional benzene until no further material was eluted. The colorless benzene eluate was evaporated to dryness under aspirator vacuum. The white, amorphous residue was crystallized from acetone and then sublimed at 150° (0.04 mm) to yield 5.0 g (25% based on **14**) of **6b**: mp 180–181° (st, under vacuum); molecular weight by mass spectral analysis is 265 (calcd for $C_{18}H_{19}NO$, 265.34); ν_{max}^{KBr} 1600 cm^{-1} (C=N); nmr (10% in $DCCl_3$) 1.11 (s, 3 H, CH_3), 1.65–2.50 (m, 4 H, aliphatic CH_2), 2.94–3.47 (m, 2 H, benzylic CH_2), 3.78–4.25 (m, C=NCH_2) and 3.90 (s, OCH_3) (total 5 H), and 7.06–8.27 (m, 5 H, aromatic H).

Anal. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.70; H, 7.30; N, 5.29.

The insoluble residue from the benzene extraction was dissolved in 800 ml of warm (50–60°) aqueous 2.5% NaOH. The NaOH solution was cooled and filtered to remove a very small quantity of insoluble residue. The solution was then made acid with dilute HCl, the acidified solution being held near 40° to prevent crystallization of what was apparently a sparingly soluble hydrochloride. The warm, acid solution was neutralized with aqueous 10% $NaHCO_3$, and the precipitated solid was sublimed at 250° (0.04 mm) to yield 2.5 g (13% based on **14**) of light yellow crystalline **6a**: mp 287–290°, with apparent decomposition (st, under vacuum); molecular weight by mass spectral[11] analysis is 251 (calcd for $C_{17}H_{17}NO$, 251.32); ν_{max}^{KBr} 1600 cm^{-1} (C=N); nmr (5% in C_5D_5N) 1.00 (s, 3 H, CH_3), 1.33–2.33 (m, 4 H, aliphatic CH_2), 2.96–3.46 (m, 2 H, benzylic CH_2), 3.68–4.49 (m, 2 H, C=NCH_2), 7.10–8.90 (m, 5 H, aromatic H), and 11.5–12.5 (b, 1 H, aromatic OH).

Anal. Calcd for $C_{17}H_{17}NO$: N, 5.62. Found: N, 5.76.

Compound **6b** (4.0 g, 0.015 mol) was boiled for 12 hr under N_2 with 50 ml of 48% HBr. The mixture was cooled and filtered through a glass-fritted funnel and the solid isolated was dissolved in 1 l. of warm (50°) aqueous 2% NaOH. The basic solution was filtered and neutralized with excess aqueous 10% $NaHCO_3$. The resulting solid was filtered, vacuum-dried, and sublimed [250° (0.04 mm)] to yield 2.9 g (77% based on **6b**) of **6a** identical with the material described above.

Preparation of 3,3a,4,5-Tetrahydro-3a-methyl-2*H*-benz[*g*]indole (7).—2-Hydroxymethylene-1-tetralone was prepared from 1-tetralone (Columbia) by the method of Campbell and coworkers.[22] 1-Tetralone (24.5 g, 0.168 mol) was converted to 27.3 g (92%) of the crude hydroxymethylene compound. The crude product was condensed with 1-butanethiol in the presence of *p*-toluenesulfonic acid to give a quantitative yield of crude 2-(*n*-butylthiomethylene)-1-tetralone. The crude thioether (21.6 g, 0.088 mol) was reductively desulfurized by the method of Ireland and Marshall[17] employing the deactivated Raney nickel described by Fieser and Fieser.[23]

The yield of 2-methyl-1-tetralone, bp 82–84° (0.6 mm) [lit.[1] bp 136–138° (16 mm)], was 17 g (94%), identical with authentic material by comparative glpc analysis.[24] The 2-methyl-1-tetralone (**16**) was converted in 98% yield to 1,2,3,4-tetrahydro-2-methyl-1-oxo-2-naphthalenepropionic acid (crude) by the method described earlier for the preparation of acid **14**. When phenanthrone **12a** was subjected to this procedure, glpc analysis revealed that a complex mixture had been produced.

The crude naphthalenepropionic acid (a viscous yellow oil)[25] was converted to benzindole **7** by the same method described earlier for the preparation of **6b**. Compound **7** was produced from the acid in 45% yield as a water-white liquid: bp 84–87° (0.04 mm); homogeneous by glpc analysis; ν_{max}^{neat} 1620 cm^{-1} (C=N); nmr (neat) 0.88 (s, 3 H, CH_3), 1.15–2.17 (m, 4 H, aliphatic CH_2), 2.20–3.15 (m, 2 H, benzylic CH_2), 3.50–4.20 (m, 2 H, C=NCH_2), 6.76–7.23 (m, 3 H, aromatic H), and 7.88–8.22 (m, 1 H, aromatic H with ortho keto function).

Anal. Calcd for $C_{13}H_{15}N$: N, 7.56. Found: N, 7.73.

Registry No.—**6a**, 28901-17-9; **6b**, 28901-18-0; **7**, 28901-19-0; **8a**, 28901-20-4; **11**, 28901-21-5; **12a**, 6299-09-8; **14**, 28901-23-7.

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(24) Appreciation is extended to Professor E. J. Eisenbraun and Dr. James M. Springer for providing the authors with an authentic sample of 2-methyl-1-tetralone.

(25) This acid was unique to this study but was not purified or fully characterized. The nmr spectrum of the acid was consistent with the proposed structure: nmr ($DCCl_3$) 1.18 (s, 3 H, CH_3), 1.76–2.61 (m, 6 H, aliphatic CH_2), 2.80–3.13 (bt, 2 H, benzylic CH_2), 7.02–7.61 (m, H, aromatic H), 7.87–8.11 (m, 1 H, aromatic H with ortho keto function), and 10.4 (s, 1 H, CO_2H).