Registry No.—**1**, 20823-96-5; (±)-**4**, 24314-85-0; (+)-(*S*)-**4**, 24314-86-1; **5**, 24214-36-6; **6** HCl, 29883-53-2; **7** HCl, 29883-54-3; **8** HCl, 29883-55-4; **9**, 29969-76-4; **10**, 29969-77-5; **11**, 29883-56-5; **13**, 19775-47-4; **14**, 29883-57-6; **15**, 29883-58-7; **16**, 29969-78-6; **16** HCl, 29883-59-8; **17** HCl, 29883-60-1.

Photochemical Synthesis of Aporphines[1]

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Received January 29, 1971

The photolysis of iodo aromatic compounds has been employed as the key step in new synthetic routes to aporphines. Photocyclization of 1-(2′-iodobenzyl)-1,2,3,4-tetrahydroisoquinoline hydrochlorides (**18**, **19**, **10**, **11**) yielded noraporphines **29** and **30** and aporphines **33** and **34** directly. Photocyclization of *N*-acyl-1-(2′-iodobenzyl)-1,2,3,4-tetrahydroisoquinolines (**14**–**17**) followed by hydrolysis gave noraporphines **25**–**28**. Photolysis of urethanes **12** and **13** afforded substituted dehydronoraporphines **23** and **24**, and two-step reduction gave (±)-aporphine (**33**) and (±)-nuciferine (**34**). Photolysis of *N*-carbophenoxy-1-(2′-iodobenzyl)-1,2,3,4-tetrahydroisoquinolines **20** and **21** followed by one-step reduction afforded good yields of (±)-aporphine (**33**) and (±)-nuciferine (**34**). The routes *via* photocyclization of *N*-acyl iodo aromatic compounds have yielded oxygenated aporphines and noraporphines in the best yields reported to date.

Aporphines, which contain the tetracyclic ring system shown in structure **33**, have been the subject of considerable chemical and pharmacological interest for many years.[3] Nevertheless, all aporphines synthesized up to 1966 were obtained only from the corresponding 1-(2′-aminobenzyl)-1,2,3,4-tetrahydroisoquinolines by way of a Pschorr-type cyclization, usually in quite low yield.[4] In 1966, two mechanistically different photochemical syntheses of aporphines were reported, one involving an oxidative stilbene–phenanthrene photocyclization,[5,6] and the other involving photocyclization of iodostilbenes to phenanthrenes.[1a,7] The present paper gives details of the photocyclization of iodobenzyltetrahydroisoquinolines to noraporphines and aporphines and an improved method for the synthesis of *N*-acyl and *N*-carbamyl noraporphines and aporphines. In addition, we now report a novel modification of the syntheses in which iodobenzylidene tetrahydroisoquinolines are cyclized to substituted dehydronoraporphines. Since the dehydronoraporphines can be readily reduced to aporphines, this method constitutes an efficient aporphine synthesis.[8]

Results

The photolysis of 1-(2′-iodobenzyl)tetrahydroisoquinolines was investigated as the most direct route to the aporphine ring system. Condensation of the appropriately substituted β-phenethylamines **1** and **2** with *o*-iodophenylacetyl chloride (**3**) gave the amides **4** and **5** (Sheme I). Bischler–Napieralski cyclization of **4** and **5** using polyphosphate ester[9] gave the 3,4-dihydroisoquinolines **6** and **7** in 93–98% yields. Direct reduction with sodium borohydride afforded the noraporphine precursors **18** and **19**, respectively. Treatment of **6** and **7** with methyl iodide followed by reduction of the stable quaternary iodides **8** and **9** with sodium borohydride gave the aporphine precursors **10** and **11**, respectively. Photolysis of **18** gave a complex intractable mixture of products which showed negligible uv absorption in the region characteristic of aporphines (270 mμ). Apparently, the presence of the free electron pair on nitrogen was detrimental to the desired photocyclization of **18**, and other reactions predominated. Salt formation was conceived as a potential method to circumvent this effect. Photolyses of the hydrochloride salts of **18**, **19**, **10**, and **11** were carried out in methanol–water mixtures in the presence of sodium bisulfite and afforded the desired noraporphines (**29** and **30**) and aporphines (**33** and **34**) in 13–20% yields (Table I). The low yield of aporphine **33** was found to be attributable to formation during the reaction of a secondary product which had the spectral characteristics of a phenanthrene. The *N*-methyl derivative of this product was shown to be identical with **22**, prepared by Hofmann degradation of aporphine **33**. This product is presumed to have resulted from cleavage of the initially formed aporphine in a manner analogous to the Hofmann reaction.

To avoid this side reaction, the photolysis of the less labile *N*-acyl precursors was investigated, with a view toward subsequent hydrolysis of the cyclization products to noraporphines. The noraporphine precursors **18** and **19** were treated with acetic anhydride–pyridine to obtain the acetamides **14** and **15** and with benzoyl chloride–pyridine to obtain the benzamides **16** and **17**, respectively. Photolysis of the *N*-acyl precursors **14**, **15**, **16**, and **17** in benzene solution in the presence of sodium thiosulfate afforded the substituted noraporphines

(1) (a) A portion of this work was reported in a preliminary communication: S. M. Kupchan and R. M. Kanojia, *Tetrahedron Lett.*, 5353 (1966). (b) This work was supported by grants from the National Institutes of Health (HE-13184 and CA-12059).

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(4) For a brief review of the synthesis of aporphines up to 1960, see A. R. Pinder in "Chemistry of Carbon Compounds," Vol. IV, E. H. Rodd, Ed., Elsevier, New York, N. Y., 1960, Chapter 25.

(5) M. P. Cava, S. C. Havlicek, A. Lindert, and R. J. Spangler, *Tetrahedron Lett.*, 2937 (1966).

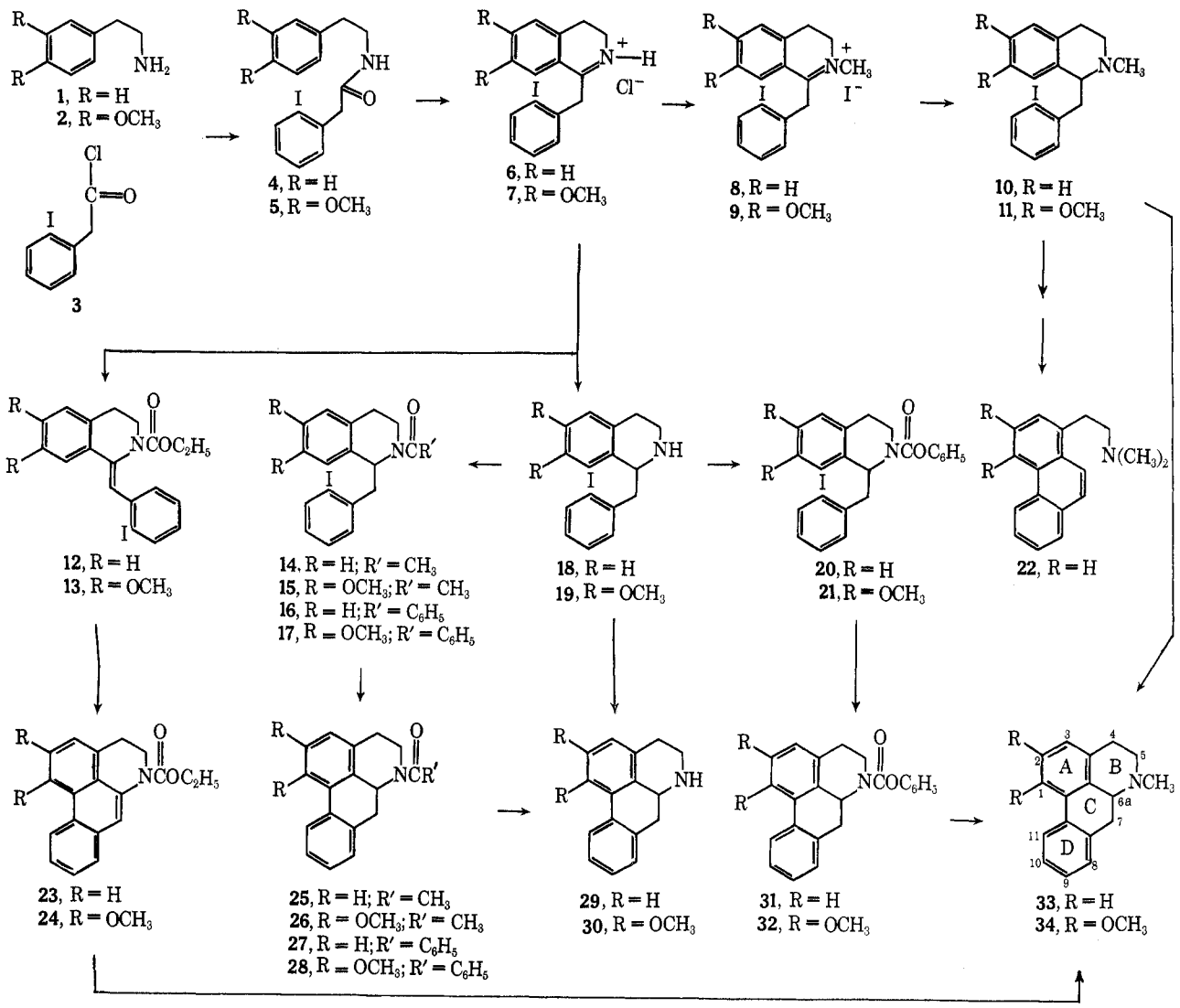
(6) N. C. Yang, G. R. Lenz, and A. Shani, *ibid.*, 2941 (1966).

(7) S. M. Kupchan and H. C. Wormser, *J. Org. Chem.*, **30**, 3792 (1965).

(8) After completion of this work, the nonoxidative photocyclization of chloro- and bromostilbene noraporphine precursors was reported: M. P. Cava, M. J. Mitchell, S. C. Havlicek, A. Lindert, and R. J. Spangler, *ibid.*, **35**, 175 (1970). The authors proposed, however, that their photocyclizations proceeded principally *via* closure to dihydrophenanthrene intermediates rather than by photochemical homolysis of the aryl halide bond involved in the photocyclization of iodostilbenes[7] [*cf.* R. K. Sharma and N. Kharasch, *Angew. Chem. Int. Ed. Engl.*, **7**, 36 (1968)].

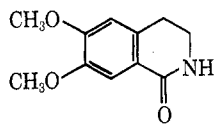
(9) Y. Kamaoka, E. Sato, O. Yonematsu, and Y. Ban, *Tetrahedron Lett.*, 2419 (1964).

SCHEME I



25, 26, 27, and 28 in 30–45% yields. Sodium thiosulfate was used to trap liberated iodine, which slowed the reaction appreciably if allowed to accumulate. Despite the possibility of solvent capture of the radical generated, high yields of intramolecular reaction products were obtained. Treatment of acetamide **25** or benzamide **27** with freshly prepared triethyloxonium fluoroborate,[10-12] followed by aqueous acid hydrolysis, gave (±)-noraporphine (**29**) in *ca.* 75% yield. Analogous treatment of the acetamide **26** and of the benzamide **28** afforded (±)-nornuciferine (**30**) in 72 and 76% yields, respectively.

In order to combine the potentially advantageous effects of intramolecular photocyclization of aryl iodides, N-acylation, and the stilbene–phenanthrene entropy factor,[7] the 1-(2′-iodobenzylidene)-2-carbethoxy-1,2,3,4-tetrahydroisoquinolines **12** and **13** were prepared for photolysis. Previous methods[13] for the preparation of this type of compound involved treating 3,4-dihydroisoquinolines with ethyl chloroformate under Schotten–Baumann conditions and gave yields of 65–75%, presumably accompanied by partially hydrolyzed starting materials. The use of an aprotic solvent with an organic base circumvented this problem. Treatment of the 3,4-dihydroisoquinolines **6** and **7** with ethyl chloroformate in pyridine gave **12** and **13** in 90% yields. These were assigned the trans configuration of the aromatic substituents about the double bond on the basis of the deshielded methyl signal at τ 9.2 in their nmr spectra.[6] Irradiation of **12** and **13** in benzene solution in the presence of sodium thiosulfate gave the desired dehydronoraporphine carbamides **23** and **24** in 41 and 67% yields (based on unrecovered starting material), respectively. The two-step conversions of **23** and **24** to (±)-aporphine[14] and (±)-nuciferine[8,15] have been reported. When urethane **13** was irradiated in methanol solution in the presence of sodium thiosulfate, 3,4-dihydro-6,7-dimethoxyisocarbostyryl (**35**) was obtained



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(12) R. F. Borch, *Tetrahedron Lett.*, 61 (1968).
(13) J. Gadamer and F. Knoch, *Arch. Pharm. (Weinheim)*, **289**, 479 (1956).
(14) B. Franck and G. Schlingloff, *Justus Liebigs Ann. Chem.*, **669**, 123 (1962); B. Franck and G. Blaschke, *ibid.*, **695**, 144 (1966).
(15) M. Shamma and W. A. Slusarchyk, *Chem. Commun.*, 528 (1965).

TABLE I

PHOTOCYCLIZATION YIELDS OF APORPHINE DERIVATIVES

Precursor	Overall yield of precursor	Photocyclization medium	Product	Yield, %
18	79	H_2O, $NaHSO_3$	(±)-Noraporphine (29)	13
19	82	H_2O, $NaHSO_3$	(±)-Nornuciferine (30)	16
10	74	H_2O, $NaHSO_3$	(±)-Aporphine (33)	18
11	73	H_2O, $NaHSO_3$	(±)-Nuciferine (34)	21
14	74	Benzene, $Na_2S_2O_3$	(±)-*N*-Acetylnoraporphine (25)	30
15	80	Benzene, $Na_2S_2O_3$	(±)-*N*-Acetylnornuciferine (26)	45
16	71	Benzene, $Na_2S_2O_3$	(±)-*N*-Benzoylnoraporphine (27)	36
17	71	Benzene, $Na_2S_2O_3$	(±)-*N*-Benzoylnornuciferine (28)	38
20	70	Benzene, $Na_2S_2O_3$	(±)-*N*-Carbophenoxynoraporphine (31)	45
21	70	Benzene, $Na_2S_2O_3$	(±)-*N*-Carbophenoxynornuciferine (32)	31
12	75	Benzene, $Na_2S_2O_3$	(±)-*N*-Carbethoxy-6*a*,7-dehydronoraporphine (23)	67
13	77	Benzene, $Na_2S_2O_3$	(±)-*N*-Carbethoxy-6*a*,7-dehydronornuciferine (24)	41

in addition to the desired dehydronoraporphine **24**. Attempts to minimize oxidative side reactions by irradiation in a nitrogen atmosphere led to drastically reduced yields of cyclized products. To circumvent the oxidative cleavage problem, the photolysis of 1-(2′-iodobenzyl)-2′-carbophenoxy-1,2,3,4-tetrahydroisoquinolines was investigated. Treatment of **18** and **19** with phenyl chloroformate in pyridine gave the urethanes **20** and **21** in 88% yield. Irradiation of **20** and **21** in benzene solution in the presence of sodium thiosulfate afforded the desired carbophenoxynoraporphines **31** and **32** in 45 and 31% yields, respectively. Since lithium aluminum hydride reductions of urethane derivatives were known to give mixtures of N–H and *N*-methyl products, Meerwein's reagent was used. The urethane **32** was treated with triethyloxonium fluoroborate in dichloromethane followed by sodium borohydride in ethanol to give (±)-nuciferine (**34**) in 75% yield. Analogous treatment of urethane **31** afforded (±)-aporphine (**33**) in 72% yield.

Discussion

While the nature of the *N*-acyl group had little effect on the extent of cyclization, solvents and trapping agents had profound effects. In order of decreasing efficiency for use in benzene, the trapping agents were thiosulfate, bisulfite, cupric acetate, and silver trifluoroacetate. In general reaction mixtures from photolyses in benzene were much cleaner than those from photolyses in methanol.

The Bischler–Napieralski route was chosen because of the high synthetic utility of the 3,4-dihydroisoquinolines. All of the precursors (**10–21**) were prepared by this route in yields from 88 to 98% for each step.

The aporphines were prepared in 19–23% overall yields *via* the urethane route. In the synthesis of (±)-nuciferine, the cyclization yield for the saturated urethane **21** (31%) is comparable to that recently obtained by nonoxidative photocyclization of a chlorostilbene analog of **13** (35%).[8] However, the latter route requires two postcyclization reduction steps of about 70% yield each, whereas the former procedure requires only one. The yields of aporphines from the Reissert synthesis and Pschorr cyclization route[16] suffer from several 70% yield reactions prior to cyclization. In general, the yield of the Pschorr reaction decreases as the oxygenation level of the precursor increases, limiting its applicability.[17,18]

The route *N*-acyl precursor → *N*-acyl noraporphine → noraporphine gave 28–33% yields of noraporphines; this appears to constitute the highest yield synthesis to date of noraporphine and nornuciferine.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are corrected. Ultraviolet spectra were determined in methanol solution on a Beckman Model DK-2A recording spectrophotometer. Nmr spectra were recorded on Varian Models A-60A and HA-100 spectrometers, in deuteriochloroform solution containing tetramethylsilane as internal standard. Infrared spectra were determined on Beckman Model IR-9 and Perkin-Elmer Models 257 and 337 recording spectrophotometers. Mass spectra were determined on Hitachi Model RMU-6E and Atlas AEI MS-902 spectrometers. Photolyses were carried out using low-pressure mercury arc lamps (2537 Å). Thin layer chromatography was carried out using silica gel F-254 and aluminum oxide F-254 (type T) analytical layer plates (Brinkman) and spots were visualized by ultraviolet light or Dragendorf spray reagent or both. Skellysolve B refers to the petroleum ether fraction of bp 60–68°. Microanalyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Mich.

N-(**β-Phenethyl**)-**2′-iodophenylacetamide** (**4**).—A solution of *o*-iodophenylacetyl chloride (**3**, 11.3 g) in chloroform (40 ml) was added dropwise to a stirred solution of β-phenylethylamine (1, 4.84 g) and triethylamine (4.04 g) in chloroform (40 ml) at 0°. The chloroform solution was stirred for 2 hr at room temperature, washed successively with 100-ml portions of water, hydrochloric acid (2.5%), and sodium bicarbonate (2.5%), dried over sodium sulfate, and evaporated. Recrystallization of the solid residue from acetone–hexane afforded 13.3 g (92%) of **4** as fine needles: mp 122–123°; λ_{max}^{KBr} 3.01, 6.10, 6.46 μ.

Anal. Calcd for $C_{16}H_{16}INO$: C, 52.81; H, 4.38; N, 3.84. Found: C, 52.91; H, 4.52; N, 3.77.

N-(**3,4-Dimethoxyphenethyl**)-**2′-iodophenylacetamide** (**5**).—A solution of homoveratrylamine (**2**, 3.2 g) and triethylamine (2.2 g) in chloroform (50 ml) at 0° was treated with *o*-iodophenylacetyl chloride (**3**, 5.0 g) and the mixture was stirred for 2 hr at room temperature. The mixture was diluted with chloroform (50 ml), washed successively with 100-ml portions of water, hydrochloric acid (2.5%), and sodium bicarbonate (2.5%), dried over sodium sulfate, and evaporated. The residue was recrystallized from acetone–hexane to give 6.4 g (90%) of **5** as rosettes: mp 137–138.5°; $\lambda_{max}^{CHCl_3}$ 6.12 (NCO) μ.

Anal. Calcd for $C_{18}H_{20}INO_3$: C, 50.82; H, 4.71; N, 3.29. Found: C, 50.89; H, 4.68; N, 3.24.

1-(2′-Iodobenzyl)-3,4-dihydroisoquinoline.—A mixture of the amide **4** (2.0 g) and polyphosphate ester (10.0 g) was heated at 130° for 3 hr. The reaction was cooled, dissolved in water

(16) J. L. Neumeyer, K. H. Oh, K. K. Weinhardt, and B. R. Neustadt, *J. Org. Chem.*, **34**, 3786 (1969).

(17) D. F. DeTar, *Org. React.*, **9**, 409 (1957).

(18) J. A. Weisbach, C. Burns, E. Macko, and B. Douglas, *J. Med. Chem.*, **6**, 91 (1963).

(50 ml), and extracted with ether (three 30-ml portions), and the aqueous layer was basified with 5 *N* NaOH and rapidly extracted with ether. The ether layer was washed with water, dried over K_2CO_3, and evaporated under a stream of nitrogen. Recrystallization from hexane gave 1.8 g (93%) of the base: mp 87–89°; HCl salt (**6**, from EtOH), mp 202–203°; nmr (DMSO-d_6) τ 6.82 (t, 2 H) and 6.10 (t, 2 H, isoquinoline CH_2), 5.22 (t, 2 H, benzylic CH_2), 3.2–2.0 (m, 8 H, aromatic).

Anal. Calcd for $C_{16}H_{18}ClIN$: C, 50.06; H, 3.93; N, 3.67. Found: C, 50.16; H, 3.98; N, 3.68.

1-(2′-Iodobenzyl)-6,7-dimethoxy-3,4-dihydroisoquinoline.—The amide **5** (2.0 g) was treated with polyphosphate ester (12.0 g) in chloroform (30 ml), and the mixture was heated to 90° for 1.5 hr, cooled, evaporated, dissolved in water, and extracted with ether. The aqueous layer was made basic with ammonium hydroxide (5 *N*) and was extracted with ether. The ether layer was dried over sodium sulfate and treated with hydrogen chloride gas. The precipitate was collected and recrystallized from methanol–ether to give **7** (2.0 g, 99%) as needles: mp 211.5–212.5°; λ_{max}^{EtOH} 227 mμ (ε 16,900), 241 (12,010), 309 (6800). Recrystallization from ethanol–isopropyl ether gave needles, mp 222–223°.

Anal. Calcd for $C_{18}H_{19}ClINO_2$: C, 48.72; H, 4.29; N, 3.16. Found: C, 48.87; H, 4.55; N, 3.09.

1-(2′-Iodobenzyl)-2-methyl-3,4-dihydroisoquinolinium Iodide (8).—A mixture of the free base of **6** (1.0 g) and methyl iodide (5 ml) was heated on a steam bath for 1 hr. The yellow precipitate was filtered and recrystallized from ethanol to give **8** (1.3 g, 92%): mp 205–207°; λ_{max}^{EtOH} 220 mμ (ε 30,000), 284 (11,700).

Anal. Calcd for $C_{17}H_{17}I_2N$: C, 41.75; H, 3.69; N, 2.86; I, 51.89. Found: C, 41.66; H, 3.64; N, 2.82; I, 51.79.

1-(2′-Iodobenzyl)-2-methyl-6,7-dimethoxy-3,4-dihydroisoquinolinium Iodide (9).—The free base of **7** was treated as above to give a product which, upon recrystallization from ethanol, yielded **9**: mp 189–191°; λ_{max}^{EtOH} 250 mμ (ε 11,400), 311 (8000), 374 (8400).

Anal. Calcd for $C_{19}H_{21}I_2NO_2$: C, 40.21; H, 4.06; N, 2.47; I, 44.79. Found: C, 40.63; H, 4.32; N, 2.61; I, 44.51.

1-(2′-Iodobenzyl)-2-methyl-1,2,3,4-tetrahydroisoquinoline (10).—A solution of iodide **8** (0.4 g) in ethanol (10 ml) was stirred with sodium borohydride (0.7 g) for 1.5 hr at 25°, the solvent evaporated, and the residue extracted with ether. The ether layer was washed with water, dried over potassium carbonate, and treated with hydrogen chloride gas to give a precipitate. Recrystallization from methanol–ether gave the hydrochloride of **10** (0.316 g, 93%) as fine needles: mp 201–202°; λ_{max}^{EtOH} 226 mμ (ε 10,300).

Anal. Calcd for $C_{17}H_{19}ClIN$: C, 51.07; H, 4.76; Cl, 8.79; I, 31.78. Found: C, 50.96; H, 4.94; Cl, 8.66; I, 31.68.

1-(2′-Iodobenzyl)-2-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (11).—A methanolic solution of **9** (0.7 g) was treated as above to yield the hydrochloride salt of **11** (0.456 g, 85%). Recrystallization from methanol–acetone gave fine needles: mp 185–187°; λ_{max}^{EtOH} 227 mμ (ε 27,800), 281 (3700), 284 (3800), 289 sh (3400).

Anal. Calcd for $C_{19}H_{23}ClINO_2$: C, 49.62; H, 5.00; N, 3.05. Found: C, 49.80; H, 5.12; N, 3.04.

1-(2′-Iodobenzyl)-1,2,3,4-tetrahydroisoquinoline (18).—A solution of the free base of **6** (1.6 g) in ethanol was stirred with sodium borohydride (2.4 g) for 1.5 hr at 25°, the solvent evaporated, and the residue dissolved in water and extracted with ether. The ether layer was washed with water, dried over potassium carbonate, and treated with hydrogen chloride gas to give a precipitate. Recrystallization from methanol–ether gave 1.536 g (93%) of **18** HCl as needles: mp 249–251°; λ_{max}^{EtOH} 226 mμ (ε 10,850), 257 (922), 264 (922), 271 (800).

Anal. Calcd for $C_{16}H_{17}ClIN$: C, 49.79, H, 4.41; N, 3.63. Found: C, 49.82; H, 4.47; N, 3.72.

1-(2′-Iodobenzyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (19).—Sodium borohydride reduction of the free base of **7** (0.85 g) in methanol by the above procedure gave 0.704 g (85%) of **19** HCl as fine needles from methanol–ether: mp 248–250°; λ_{max}^{EtOH} 226 mμ (ε 17,200), 281 (4800), 284 (4800).

Anal. Calcd for $C_{18}H_{21}ClINO_2$: C, 48.51; H, 4.72; Cl, 7.95; I, 28.36; N, 3.14. Found: C, 48.54; H, 4.90; Cl, 7.91; I, 28.44; N, 3.19.

1-(2′-Iodobenzyl)-2-acetyl-1,2,3,4-tetrahydroisoquinoline (14).—A mixture of **18** (0.41 g), acetic anhydride (1 ml), and pyridine (1.5 ml) was allowed to stand at room temperature overnight. The solution was poured over ice and sodium carbonate, extracted with chloroform (50 ml), washed with 40-ml portions of sodium hydroxide (2%), hydrochloric acid (2.5%), and water, dried over sodium sulfate, and evaporated. The residue was chromatographed on silica gel plates (preparative) to give **14** as a homogeneous oil (0.45 g, 90%): $\lambda_{max}^{CHCl_3}$ 6.10 μ (NC=O); nmr τ 7.94 and 8.58 (*N*-acetyl methyl, two conformations); mass spectrum *m/e* 396 (M^+), 353 (M − acetyl).

1-(2′-Iodobenzyl)-2-acetyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (15).—A solution of **19** (1.0 g) in pyridine (25 ml) and acetic anhydride (0.29 ml) was allowed to stand at 25° for 18 hr and was then poured onto ice and hydrochloric acid and extracted with chloroform. The chloroform extract was washed with 2 *N* sodium hydroxide, 2 *N* hydrochloric acid, and water, dried over sodium sulfate, and evaporated to dryness. The residue was recrystallized from benzene–hexane to give **15** (1.08 g, 98%) as needles: mp 101–102°; $\lambda_{max}^{CHCl_3}$ 6.19 μ (NC=O); mass spectrum *m/e* 234, 192; nmr τ 8.5 (s, 3 H, acetate methyl), 6.08 (s, 6 H, 2 OCH_3).

Anal. Calcd for $C_{20}H_{22}INO_3$: C, 53.21; H, 4.87; N, 3.10. Found: C, 53.39; H, 5.03; N, 3.20.

1-(2′-Iodobenzyl)-2-benzoyl-1,2,3,4-tetrahydroisoquinoline (16).—A solution of **18** hydrochloride (0.7 g) and benzoyl chloride (1.0 g) in pyridine (4.5 ml) was treated as above to yield an oil which was crystallized from benzene–Skellysolve B to give **16** (0.8 g, 89%) as needles: mp 140–141°; λ_{max}^{KBr} 6.18 μ (NC=O); λ_{max}^{EtOH} 263 mμ (ε 2050), 272 (1500); mass spectrum *m/e* 453 (M^+), 348, 236, 131.

Anal. Calcd for $C_{23}H_{20}INO$: C, 60.94; H, 4.42; N, 3.09. Found: C, 61.07; H, 3.93; N, 2.77.

1-(2′-Iodobenzyl)-2-benzoyl-6,7-dimethoxy-3,4-dihydroisoquinoline (17).—A mixture of **19** (0.46 g), pyridine (2.5 ml), and benzoyl chloride (0.34 ml) was treated as above and the residue on recrystallization from benzene–hexane gave **17** (0.48 g, 80%) as prisms: mp 133–134°; mass spectrum *m/e* 408, 296, 105; nmr τ 6.18 (s) and 6.08 (s) (2 × 3 H, OCH_3), 2.0–3.2 (9 H, aromatic); λ_{max}^{KBr} 6.19 μ (NC=O); λ_{max}^{EtOH} 263 mμ (ε 1930), 272 (1400).

Anal. Calcd for $C_{25}H_{24}INO_3$: C, 58.48; H, 4.68; N, 2.73. Found: C, 58.49; H, 4.72; N, 2.66.

1-(2′-Iodobenzyl)-2-carbophenoxy-1,2,3,4-tetrahydroisoquinoline (20).—A solution of **18** (0.2 g) and triethylamine (1 ml) in chloroform (25 ml) was cooled to 0° and phenyl chloroformate (0.85 ml) was added. The mixture was allowed to warm to room temperature and was then heated to 40° for 2 hr. The solution was diluted with chloroform (50 ml) and washed with 3% hydrochloric acid, 3% sodium bicarbonate, and water, dried over sodium sulfate, and evaporated to dryness. Chromatography on alumina afforded a residue which was recrystallized from benzene–hexane to give **20** (0.218 g, 88%) as fine needles: mp 151–152°; λ_{max}^{KBr} 5.86 μ (NCOOR); mass spectrum *m/e* 348, 252, 131; nmr τ 2.0–3.5 (m, 13 H, aromatic).

Anal. Calcd for $C_{23}H_{20}INO_2$: C, 58.84; H, 4.26; N, 3.00. Found: C, 59.03; H, 4.37; N, 2.99.

1-(2′-Iodobenzyl)-2-carbophenoxy-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (21).—A solution of **19** (0.19 g) and triethylamine (0.85 ml) in chloroform (25 ml) was cooled to 0° and phenyl chloroformate (0.7 ml) was added. The mixture was treated as above to yield a residue which, after alumina chromatography and recrystallization from benzene–hexane, afforded **21** (0.196 g, 87%) as needles: mp 160–161°; λ_{max}^{KBr} 5.83 μ (NCOOR); mass spectrum *m/e* 408, 312, 191; nmr τ 6.15 (s) and 6.10 (s) (2 × 3 H, OCH_3), 3.3 (s, 1 H), 3.1 (s, 1 H), 2.8 (m, 8 H), 2.1 (m, 1 H, aromatic).

Anal. Calcd for $C_{25}H_{24}INO_4$: C, 56.71; H, 4.53; N, 2.64. Found: C, 56.78; H, 4.64; N, 2.71.

1-(2′-Iodobenzylidene)-2-carbethoxy-1,2,3,4-tetrahydroisoquinoline (12).—A solution of the 3,4-dihydroisoquinoline hydrochloride **6** (2.43 g) in chloroform (40 ml) and pyridine (8 ml) was cooled to −10°, and ethyl chloroformate (12 ml) was added dropwise. The mixture was allowed to warm to room temperature slowly and was stirred at 40° for 2 hr. The solution was cooled, diluted with chloroform (50 ml), extracted with 100-ml portions of hydrochloric acid (2.5%), aqueous sodium bicarbonate (2.5%), and water, and dried over sodium sulfate. Chromatography on a silica gel column yielded **12** (2.34 g, 89%) as light yellow plates: mp 92–93°; λ_{max}^{KBr} 5.83 μ (NCOOR); λ_{max}^{EtOH} 293 mμ (ε 26,600); nmr τ 9.20 (t, 3 H, CH_3CH_2), 6.35 (q, 2 H, J = 7 Hz, CH_3CH_2–), 3.2–2.0 (9 H, aromatic); mass spectrum *m/e* 419 (M^+), 346 ($M^+ - CO_2Et$).

Anal. Calcd for $C_{19}H_{18}INO_2$: C, 54.41, H, 4.29; N, 3.35. Found: C, 54.35; H, 4.33; N, 3.30.

1-(2′-Iodobenzylidene)-2-carbethoxy-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (13).—A solution of the 3,4-dihydroisoquinoline hydrochloride **7** (2.32 g) in chloroform (40 ml) and pyridine (7 ml) was cooled to −20° and ethyl chloroformate (10.85 g) was added dropwise. The mixture was stirred for 2 hr at 25° and for 1 hr at 40°, diluted with chloroform (50 ml), extracted with 100 ml each of 2.5% hydrochloric acid, 2.5% aqueous sodium bicarbonate, and water, dried over sodium sulfate, and evaporated. Chromatography on alumina (neutral) gave a residue which on recrystallization from benzene–Skellysolve B afforded **13** (2.25 g, 90%) as platelets: mp 135–136°; λ_{max}^{KBr} 5.93 μ (NCOOR); λ_{max}^{EtOH} 221 mμ (ε 32,900), 298 (15,750), 322 (18,100); nmr τ 9.18 (t, 3 H, CH_3CH_2), 6.03 (s), 6.10 (s) (2 × 3 H, OCH_3).

Anal. Calcd for $C_{21}H_{22}INO_4$: C, 52.61; H, 4.59; N, 2.90. Found: C, 52.76; H, 4.74; N, 3.05.

Noraporphine (29). A. From Photolysis.—A solution of the hydrochloride salt of **18** (0.5 g) and sodium bisulfite (0.15 g) in water (1.0 l.) was irradiated for 18 hr and evaporated. The residue was made basic with ammonium hydroxide and extracted with chloroform. The chloroform extract was chromatographed on silica gel using chloroform–methanol mixtures to yield a homogeneous oily fraction (0.15 g). Conversion to the hydrochloride salt and recrystallization from acetone–methanol gave **29** HCl (0.14 g, 33%): mp 275–280° dec; λ_{max}^{EtOH} 270 mμ (ε 19,300) [lit.[19] mp 284° dec; λ_{max}^{EtOH} 270 mμ (ε 18,200)].

B. From Hydrolysis of 25.—A solution of the acetamide **25** (50 mg) in dichloromethane (5 ml) was treated with freshly prepared triethyloxonium fluoroborate (0.12 g) and the mixture was stirred for 42 hr. The solution was evaporated and 3% acetic acid in dioxane (6 ml) was added. The mixture was warmed to 40° for 12 hr, diluted with aqueous sodium hydroxide (2%), and extracted with ether. The ether layer was dried over sodium sulfate and treated with hydrogen chloride gas. The resulting precipitate was collected and recrystallized from methanol–acetone to give **29** HCl (31 mg, 74%), mp 282–284° dec, identical in all respects (ir, uv, nmr, tlc, mass spectrum, mixture melting point) with a sample of (±)-noraporphine prepared by the above method.

C. From Hydrolysis of 27.—A solution of the benzamide **27** (50 mg) in dichloromethane (2 ml) was treated with triethyloxonium fluoroborate (0.05 g) for 36 hr. The mixture was worked up as above to give, after acidification and recrystallization, **29** HCl (29.8 mg, 75%), mp 282–285°, identical with that obtained above by ir, mass spectral, and mixture melting point determinations.

Nornuciferine (30). A. From Photolysis.—A solution of the hydrochloride salt of **19** (0.4 g) and sodium bisulfite (0.13 g) in water (1.0 l.) was irradiated for 12 hr, the solvent removed, and the residue purified as above. Recrystallization of the hydrochloride salt from methanol–ether gave **30** (0.058 g, 21%), mp 260–262° dec (lit.[20] mp 261–262° dec). The infrared spectra of **30** and of an authentic sample of nornuciferine (from *Nelumbo lutea*) in chloroform solution were identical.

B. From Hydrolysis of 28.—A solution of the benzamide **28** (60 mg) in dichloromethane (5 ml) was treated with triethyloxonium fluoroborate (0.1 g) and the mixture was stirred under nitrogen for 36 hr. The solution was evaporated and the residue was dissolved in 3% acetic acid in dioxane, stirred for 18 hr at 40°, diluted with aqueous sodium hydroxide (2%), and extracted with ether. The ether solution was dried over sodium sulfate and treated with hydrogen chloride gas. The precipitate was collected and recrystallized from methanol–ether to give **30** HCl (38 mg, 76%): mp 260–262° dec, mass spectrum *m/e* 281 (M^+). Infrared spectra of samples of **30** and an authentic specimen of (−)-nornuciferine from *Nelumbo lutea*, measured in chloroform, were superimposable.

C. From Hydrolysis of 26.—A solution of the acetamide **26** (50 mg) in dichloromethane (5 ml) was treated with triethyloxonium fluoroborate (0.1 g) and treated as above to yield **30** HCl (35.2 mg, 72%) as needles, mp 260–262°, identical (ir, tlc, mass spectrum, mixture melting point) with that obtained above.

Aporphine (33). A. From Photolysis.—A solution of the hydrochloride salt of **10** (0.2 g) and sodium bisulfite (0.052 g) in water (20 ml) and methanol (180 ml) was irradiated for 12 hr and the solvent evaporated; the residue was made basic with ammonium hydroxide (5%) and extracted with chloroform. The chloroform layer was washed with water, dried (Na_2SO_4), evaporated, and chromatographed on silica gel plates using 12% methanol in chloroform, to give two materials. The higher R_f material showed the characteristic aporphine uv spectrum and was rechromatographed, converted to the hydrochloride salt, and recrystallized from methanol–acetone to give **33** (0.018 g, 13%): mp 253–255°; λ_{max}^{EtOH} 270 mμ (ε 18,520), 282 (15,400) [lit.[18] mp 255°; λ_{max}^{EtOH} 270 mμ (ε 18,600), 282 (15,490)].

B. From Reduction of 31.—A solution of carbamate **31** (0.05 g) in dichloromethane (6 ml) was treated with freshly prepared triethyloxonium fluoroborate (0.12 g) and was stirred for 38 hr at 25°. The solvent was removed *in vacuo*, ethanol (6 ml) was added, and the solution was cooled to 0°. Sodium borohydride (0.2 g) was added in portions and the mixture was stirred overnight, evaporated, dissolved in water, and extracted with ether (three 50-ml portions). The ether extract was dried over sodium sulfate, concentrated to 25 ml, and treated with hydrogen chloride gas. The resulting precipitate was filtered and recrystallized from methanol–acetone to give **33** HCl (38 mg, 72%), mp 253–255°, indistinguishable from that obtained above by ir, nmr, mass spectrum, and mixture melting point.

***N,N*-Dimethyl-β-(1-phenanthryl)ethylamine Hydrochloride (22). A. From the Photolysis of 10.**—A second product of the mixture from the photolysis of **10** was obtained by silica gel chromatography as an oil and was converted to its hydrochloride salt. This material had a diffuse melting point and showed λ_{max}^{EtOH} 296 mμ (ε 15,000), 255 (60,900), 248 (45,000). The hydrochloride salt was dissolved in methanol (15 ml) and stirred with 37% formalin (0.5 ml) at 25° for 30 min. Sodium borohydride (0.1 g) was added and stirring was continued for 1 hr. The solvent was evaporated, and the residue was made basic and extracted with chloroform. The chloroform layer was evaporated, the residue dissolved in ether, and hydrogen chloride gas added. The precipitate was recrystallized from methanol–acetone to give the hydrochloride of **22**: mp 237° (sealed tube); λ_{max}^{EtOH} 298 mμ (ε 16,100), 286 (12,400), 276 (13,000), 255 (62,000), 248 (48,400), 221 (20,000).

B. By Hofmann Degradation of 33.—A mixture of methyl iodide (0.3 ml) and aporphine **33** (0.04 g) was heated under reflux on a steam bath for 3 hr, the excess methyl iodide was evaporated under N_2, methanol (10 ml) and potassium hydroxide (2 g) were added, and the mixture was again heated under reflux for 3 hr. The solvent was evaporated and the residue partitioned between water and chloroform. The chloroform layer was washed with water, dried over sodium sulfate, treated with hydrogen chloride gas, and evaporated; the residue recrystallized from methanol–acetone to give the hydrochloride of **22** (0.02 g), mp 239° (sealed tube). The infrared spectra in chloroform solution of the salts derived from both routes were superimposable. The nmr spectrum showed τ 7.67 [s, 6 H, $N(CH_3)_2$], 6.72 (t, 2 H, NCH_2), 7.40 (t, 2 H, benzylic CH_2), 1.43 (m, 2 H, C-4, C-5), 2.0–3.6 (m, 7 H, aromatic).

Anal. Calcd for $C_{18}H_{20}ClN$: C, 75.62; H, 6.70; N, 4.90. Found: C, 75.52; H, 6.75; N, 4.84.

(±)-Nuciferine (34). A. From Photolysis.—A solution of the hydrochloride salt of **11** (0.2 g) in water (0.5 l.) containing sodium bisulfite (0.052 g) was irradiated for 10 hr, and the solvent was removed under reduced pressure, made basic with ammonium hydroxide (5%), and extracted with chloroform. The chloroform layer was washed with water, dried over sodium sulfate, evaporated, and chromatographed on silica gel using chloroform–methanol (0–12%) mixtures to give **34** HCl (0.024 g, 16%), mp 257° dec. The infrared spectrum of **22** was superimposable on that of an authentic sample of nuciferine.

B. From Reduction of 32.—A solution of the carbamate **32** (50 mg) and triethyloxonium fluoroborate (0.2 g) in dichloromethane (2 ml) was stirred at room temperature overnight, evaporated under a stream of nitrogen, and treated with ethanol (15 ml) and sodium borohydride (0.2 g). The mixture was stirred at room temperature for 12 hr, heated to 40° for 2 hr, evaporated, dissolved in water (30 ml), and extracted with ether (three 30-ml portions). The ether extract was dried over potassium carbonate, concentrated to 25 ml, and treated with hydrogen chloride. The resulting precipitate was collected and recrystallized from chloroform–methanol to give **34** HCl (30 mg, 75%), mp 256–257°. The infrared spectra of **34** and an authentic sample of nuciferine from *Nelumbo lutea*, measured in chloroform, were superimposable.

(19) E. Ochiai and J. Kuniyoshi, *Pharm. Bull.*, **5**, 292 (1967).

(20) J. A. Weisbach and B. Douglas, *J. Org. Chem.*, **27**, 3738 (1962).

C. From Reduction of 24.—A solution of the dehydroaporphine **24** (0.2 g) in ether–THF (1:1) was added dropwise to a stirred slurry of lithium aluminum hydride (86 mg) in dry ether at room temperature. The mixture was stirred for 8 hr, the excess reagent decomposed with wet ether, and the solution dried over sodium sulfate. Hydrogen chloride gas was added and the solvent was removed *in vacuo*. The residue (0.188 g) was dissolved in 80% acetic acid (30 ml) and stirred with platinum oxide catalyst (120 mg) in a hydrogenator at 1 atm pressure for 18 hr. The filtrate from the hydrogenation was basified and extracted with ether. The ether was evaporated and the residue was chromatographed on silica gel preparative layer plates to give **34** (73 mg, 51%) as needles from chloroform–hexane: mp 141°; λ_{max}^{MeOH} 230 mμ (ε 18,000), 272 (14,500), 310 (2000). The infrared spectra of a sample of **34** and authentic nuciferine in chloroform solution were superimposable.

***N*-Acetylnoraporphine (25).**—Irradiation of a solution of **14** (0.19 g) and sodium thiosulfate (0.19 g) in benzene (100 ml) and water (1 ml) for 12 hr, followed by evaporation and silica gel chromatography using chloroform, afforded a solid which was recrystallized from chloroform–methanol to yield **25** (0.04 g, 31%), mp 214°. Recrystallization from benzene–Skellysolve B gave needles: mp 215°; λ_{max}^{EtOH} 271 mμ (ε 18,600); λ_{max}^{KBr} 6.12 μ (*N*-acetyl); nmr τ 7.79 (s, 3 H, acetyl methyl), 6.5–7.5 (m, 7 H, CH_2), 2.0–3.0 (m, 7 H, aromatic); mass spectrum *m/e* 263 (M^+), 220 (M^+ − acetyl).

Anal. Calcd for $C_{18}H_{17}NO$: C, 82.32; H, 6.61; N, 5.65. Found: C, 82.13; H, 6.46; N, 5.32.

***N*-Acetylnornuciferine (26).**—A solution of **15** (70 mg) and sodium thiosulfate (70 mg) in benzene (75 ml) and water (1 ml) was irradiated for 12 hr and worked up as above. Chromatography and recrystallization from benzene–hexane gave **26** (23 mg, 44%) as rosettes: mp 232–233°; λ_{max}^{KBr} 6.17 μ (NCO); mass spectrum *m/e* 291 (M^+), 248 (M^+ − acetyl); λ_{max}^{EtOH} 274 mμ (ε 32,100); nmr τ 7.81 (s, 3 H, $NCOCH_3$), 6.33 (s) and 6.12 (s) (2 × 3 H, OCH_3), 3.32 (s, 1 H, C-5), 1.57 (m, 1 H, C-11), 2.69 (m, 4 H, aromatic). These data were in good agreement with those previously reported.[21,22]

***N*-Benzoylnoraporphine (27).**—Irradiation of a solution of **16** (0.14 g) and sodium thiosulfate (0.14 g) in benzene (100 ml) and water (1 ml) and purification as above gave **27** (0.032 g, 36%) from methanol as needles: mp 201–202°; λ_{max}^{KBr} 6.19 μ (NCO); λ_{max}^{EtOH} 269 mμ (ε 19,550); mass spectrum *m/e* 325 (M^+), 220.

Anal. Calcd for $C_{23}H_{19}NO$: C, 84.67; H, 6.28; N, 4.29. Found: C, 84.80; H, 6.32; N, 4.24.

***N*-Benzoylnornuciferine (28).**—A solution of **17** (0.4 g) and sodium thiosulfate (0.15 g) in benzene (100 ml) and water (2 ml) was irradiated for 12 hr. The benzene layer was washed with water, evaporated, and chromatographed on silica gel plates to afford a solid residue. Recrystallization from acetone–Skellysolve B gave **28** (0.116 g, 38%) as prisms: mp 193–194°; λ_{max}^{KBr} 6.19 μ (amide CO); λ_{max}^{EtOH} 271 mμ (ε 21,800); mass spectrum *m/e* 385 (M^+), 280 (M^+ − benzoyl).

Anal. Calcd for $C_{25}H_{23}NO_3$: C, 77.90; H, 6.01; N, 3.63. Found: C, 77.74; H, 6.02; N, 3.52.

***N*-Carbophenoxynoraporphine (31).**—A solution of **20** (0.1 g) and sodium thiosulfate (0.1 g) in benzene (100 ml) and water (1 ml) was irradiated for 9 hr. Evaporation and chromatography on silica gel using chloroform as eluent gave a light yellow oil which was crystallized from methanol. Recrystallization from chloroform–methanol gave **31** (0.032 g, 45%) as rosettes: mp 212–213°; λ_{max}^{KBr} 5.83 μ (NCOOR); nmr τ 7.01 (t, 2 H, *J* = 6 Hz), 6.8 (t, 2 H, *J* = 6 Hz), 2.7 (m, 11 H, aromatic), 1.7 (m, 1 H, C-11 proton); mass spectrum *m/e* 341 (M^+), 264, 220.

Anal. Calcd for $C_{23}H_{19}NO_2$: C, 80.91; H, 5.61; N, 4.10. Found: C, 80.76; H, 5.64; N, 3.99.

(21) I. Baxter and G. Swan, *J. Chem. Soc.*, 4014 (1965).

(22) D. R. Dalton, M. P. Cava, and K. T. Buck, *Tetrahedron Lett.*, 2687 (1965).

***N*-Carbophenoxynornuciferine (32).**—A solution of **21** (0.096 g) and sodium thiosulfate (0.100 g) in benzene (100 ml) and water (1 ml) was irradiated for 10 hr. The reaction mixture was evaporated and chromatographed in silica gel using chloroform as eluent; the light tan residue obtained was recrystallized from methanol to yield **32** (0.025 g, 31%) as rosettes: mp 205–206°; λ_{max}^{KBr} 5.83 μ (NCOOR); nmr τ 6.10 (s) and 6.32 (s) (2 × 3 H, OCH_3), 3.30 (s, 1 H, C-5), 2.5–3.0 (m, 9 H, aromatic), 1.5 (m, 1 H, C-11); mass spectrum *m/e* 401 (M^+), 263, 249, 235 amu.

Anal. Calcd for $C_{25}H_{23}NO_4$: C, 74.49, H, 5.78; N, 3.49. Found: C, 74.54; H, 5.83; N, 3.36.

***N*-Carbethoxy-6a,7-dehydronoraporphine (23).**—A mixture of the stilbene **12** (0.158 g) and sodium thiosulfate (0.158 g) in benzene (75 ml) and water (3 ml) was irradiated for 11 hr. The benzene layer was evaporated and chromatographed on silica gel (preparative) layer plates to give two fractions, A and B. Fraction A was crystallized from benzene–Skellysolve B to give **23** (0.056 g): mp 92–93°; mass spectrum *m/e* 291 (M^+), 263, 218; λ_{max}^{KBr} 5.93 μ (carbamate ester); λ_{max}^{MeOH} 254 mμ (ε 8000), 261 (9300), 304 (3000); nmr τ 8.66 (t, 3 H, *J* = 7 Hz), 1.90–2.80 (m, 6 H, aromatic), 1.4 (d, 2 H, C-1 and C-11).

Anal. Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.38; H, 5.74; N, 4.78.

Fraction B was crystallized from benzene–Skellysolve B to give 36 mg of the unreacted starting material **12**, mp 91–92°. The yield of **23** (calculated on the basis of unrecovered starting material) was 67%.

***N*-Carbethoxy-6a,7-dehydronornuciferine (24).**—A solution of the stilbene **13** (0.25 g) and sodium thiosulfate (0.25 g) in benzene (100 ml) and water (2.5 ml) was irradiated for 14 hr. The benzene solution was evaporated and the residue chromatographed on a silica gel column using chloroform containing 1.5% methanol to give **24** (0.068 g, 36.5%) as prisms: mp 129–130°; λ_{max}^{KBr} 5.92 μ (carbamate ester); λ_{max}^{MeOH} 254 mμ (ε 44,200), 260 (44,700), 310 (8150), 321 (8250), 353 (950); nmr τ 8.72 (t, 3 H, *J* = 7 Hz), 6.82 (t, 2 H, *J* = 6 Hz), 5.92 (t, 2 H, *J* = 6 Hz), 5.68 (q, 2 H, *J* = 7 Hz), 6.0 (s, 3 H), 6.08 (s, 3 H), 2.92 (s, 1 H), 2.1–2.5 (m, 4 H), 0.41 (m, 1 H).

Anal. Calcd for $C_{21}H_{21}NO_4$: C, 71.79; H, 5.98; N, 3.98. Found: C, 71.82; H, 6.01; N, 3.95.

Later fractions eluted from this column yielded a residue which was recrystallized from benzene–Skellysolve B to give 0.026 g (10%) of unreacted starting material, mp 135–136°. The yield of **24** calculated on the basis of unrecovered **13** was 41%.

Portionwise photolysis of the stilbene **13** (7.2 g) in methanol (5.5 l.) solution containing water (60 ml) and sodium thiosulfate (2.4 g) for 16 hr and work-up as above gave 1.82 g of crude product. This residue was chromatographed on silicic acid and neutral alumina columns using 1% methanol in chloroform as eluent to afford the desired dehydronoraporphine **24** (0.36 g), identical with that obtained above. A second product (0.075 g), after recrystallization from ethyl acetate, showed mp 172–173°, and was identified as 3,4-dihydro-6,7-dimethoxyisocarbostyryl (**35**) by its melting point (lit.[23] 175°) and ir, uv, and nmr characteristics.

Registry No.—**4**, 14528-35-9; **5**, 30237-85-5; **6**, 14528-36-0; **6** HCl, 14528-37-1; **7** HCl, 30237-88-8; **8**, 14645-27-3; **9**, 30237-90-2; **10** HCl, 30256-05-4; **11** HCl, 30256-06-5; **12**, 30237-91-3; **13**, 30237-92-4; **14**, 30256-07-6; **15**, 30256-08-7; **16**, 30256-09-8; **17**, 30256-10-1; **18** HCl, 30256-11-2; **19** HCl, 30256-12-3; **20**, 30256-13-4; **21**, 30256-14-5; **22** HCl, 30237-93-5; **23**, 7630-70-8; **24**, 13555-30-1; **25**, 30256-36-1; **26**, 29424-85-9; **27**, 30256-37-2; **28**, 30256-38-3; **31**, 30256-39-4; **32**, 30256-40-7; **34** HCl, 5868-18-8.

(23) K. Wiesner, Z. Valenta, A. J. Manson, and F. W. Stonner, *J. Amer. Chem. Soc.*, **77**, 675 (1955).