of N-allylnormorphine hydrochloride, but was negative (green) for both apomorphine hydrochloride and for **1**. The nitric acid color test[18b] for apomorphine was negative (orange-red) for N-allylnormorphine hydrochloride but was positive (purple) for apomorphine hydrochloride and for **1**. N-Allylnormorphine hydrochloride melted at 265–266° with frothing, when placed in the melting point apparatus 5° below its melting point (lit. m.p. 260–263° [18a] and 269° dec.[19]). Compound 1 melted at 244–245° with frothing, and a mixture of the two compounds melted gradually, beginning at approximately 220°, under similar conditions. A Karl Fischer determination[20] indicated no physically or chemically bound water in **1**; $\alpha^{30}D$ −64.0° (*c* 0.328, water).

Anal. Calcd. for $C_{19}H_{20}ClNO_2$: C, 69.10; H, 6.11; Cl, 10.74; N, 4.25. Found: C, 68.83; H, 5.89; Cl, 10.32; N, 4.22.

O,O′-Dimethylapomorphine methiodide was obtained in 68% yield by the method of Späth and Hromatka,[21] except that apomorphine base was not used. A suspension of apomorphine hydrochloride (S. B. Penick and Co.) in methanol was treated, under nitrogen, with an equimolecular amount of methanolic NaOH, and an ethereal solution of diazomethane was added to the resulting solution. The product was a light brown oil. Späth and Hromatka[21] reported a light yellow oil. No reliable physical data were found in the literature for this compound, and it was characterized as its methiodide salt. To a solution of 0.41 g. of the oil in 20 ml. of anhydrous ether was added 1 ml. of methyl iodide. The precipitate which separated was collected on a filter, washed several times with anhydrous ether, and the resulting product (0.06 g., 99%) was dissolved in hot anhydrous ethanol. It was recrystallized by addition of anhydrous ether; m.p. 188–190°, lit.[3] m.p. 195°.

O,O′-Dimethyl-N-allylnorapomorphine was obtained by a modification of the method of Späth and Hromatka[21] for the preparation of O,O′-dimethylapomorphine. Compound **1** (0.34 g.) was suspended in 5 ml. of anhydrous methanol in a flask immersed in an ice bath. Nitrogen was passed through the stirred suspension, and 0.04 g. of NaOH in 5 ml. of anhydrous methanol was added slowly. To this mixture was added an excess of ethereal CH_2N_2; the reaction flask was kept in the ice bath 1 hr. and at room temperature 11 hr. Half of the solvent was removed, and the concentrate was treated with an excess of ethereal diazomethane. It was left for 12 hr. Evaporation of the solvent (steam bath) yielded an oily residue which was dissolved in 15 ml. of cold 1 *N* HCl and transferred to a separatory funnel. Sufficient cold 50% NaOH was added to make the solution strongly alkaline, and it was shaken with 200 ml. of ether in divided portions. The combined ether extracts were washed once with 50% NaOH and once with water. The ether was removed, and the residue was stored in a desiccator under reduced pressure for several hours. The dried material was dissolved in anhydrous ether, the solution was filtered through sintered glass, and the ether was removed. The residue (0.223 g., 70%) was a light brown, viscous oil, $n^{24}D$ 1.6131.

Anal. Calcd. for $C_{21}H_{23}NO_2$: C, 78.50; H, 7.17; N, 4.36. Found: C, 78.25; H, 7.18; N, 4.20.

O,O′-Dimethyl-N-allylapomorphinium Iodide (2). A. From O,O′-Dimethylapomorphine.—To 0.075 g. of O,O′-dimethylapomorphine in 20 ml. of anhydrous ether was added 1 ml. of allyl iodide (Eastman White Label) which had been distilled twice, protected from strong light, and stored in the dark. The solution was left in the dark for 3 hr. The solid which separated was collected on a filter and washed several times with anhydrous ether. The resulting product (0.11 g., 95%) was dissolved in hot anhydrous ethanol and recrystallized by addition of anhydrous ether; this procedure was repeated four times. The pale yellow microcrystalline product softened at approximately 154° and melted at 168–170° with frothing.

Anal. Calcd. for $C_{22}H_{26}INO_2$: C, 57.02; H, 5.62; I, 27.43; N, 3.02. Found: C, 57.00; H, 5.50; I, 27.59; N, 3.03.

B. From O,O′-Dimethyl-N-allylnorapomorphine.—O,O′-Dimethyl-N-allylnorapomorphine (0.015 g.) in 20 ml. of anhydrous ether was mixed with 1 ml. of methyl iodide and left for 3 hr. The solid which separated was collected on a filter and washed several times with anhydrous ether. The resulting product (0.02 g., 94%) was dissolved in hot anhydrous ethanol and recrystallized by addition of anhydrous ether; this procedure was repeated three times. The pale yellow microcrystalline product softened at approximately 150° and melted at 166–169° with frothing.

Anal. Calcd. for $C_{22}H_{26}INO_2$: C, 57.02; H, 5.62. Found: C, 57.30; H, 5.27.

A mixture melting point determination of the products of A and B showed no depression. The infrared spectra (Nujol) of A and B were superimposable.

(19) "The Merck Index," 7th Ed., Merck and Co., Inc., Rahway, N. J., 1960, p. 701.

(20) Performed by Huffman Microanalytical Laboratories, Wheatridge, Colo.

(21) E. Späth and O. Hromatka, *Ber.*, **62**, 325 (1929).

Constitution and Analgetic Activity of a New Product in the Benzomorphan Synthesis

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Cyclization of 3,4-diethyl-2-(*p*-hydroxybenzyl)-1-methyl-1,2,5,6-tetrahydropyridine (I) hydrochloride with aluminum bromide has given a mixture of α- and β-5,9-diethyl-2′-hydroxy-2-methyl-6,7-benzomorphans (II and III) and 1,5-dimethyl-4-ethyl-7-hydroxy-1,2,3,4,5,10,11,12-octahydrobenzo[*g*]quinoline (IV) in yields of 19, 14, and 27%, respectively. The structure of IV was proved by n.m.r. and mass spectrometry, and by degradation to 7-methoxy-1-methylnaphthalene. When I was cyclized with 85% phosphoric acid at 185°, II (50%) and III (25%) but no IV were obtained. The analgetic potency of IV is about half that of II, between morphine and codeine.

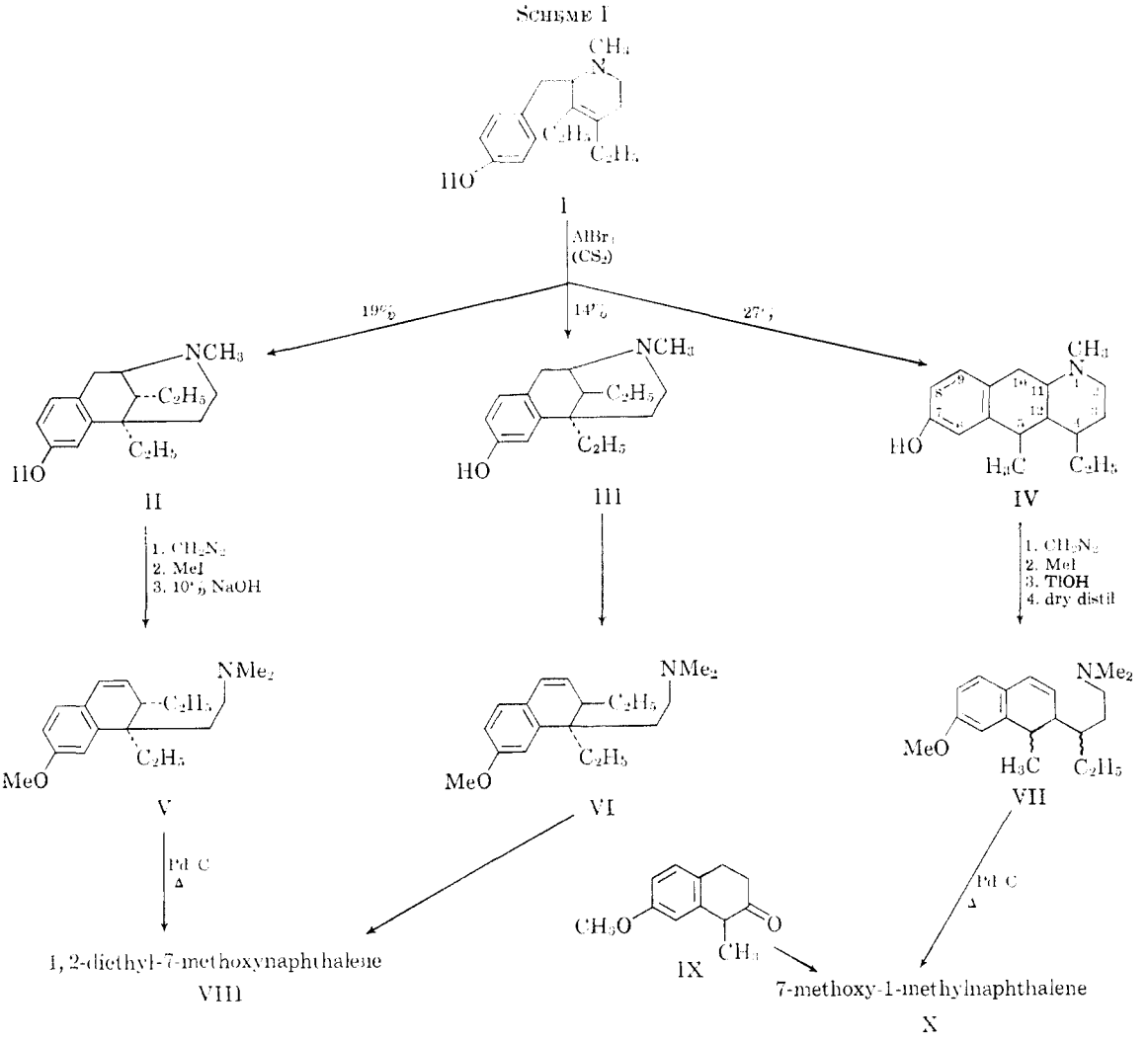
In the course of attempts to improve the yield of β-5,9-diethyl-2′-hydroxy-2-methyl-6,7-benzomorphan (III), a very potent analgetic with a favorable therapeutic ratio,[2] aluminum bromide cyclization of 3,4-diethyl-2-(*p*-hydroxybenzyl)-1-methyl-1,2,5,6-tetrahydropyridine (I) hydrochloride was found to yield a mixture of three[3] easily separable, well-defined products (see Scheme I). They are α- and β-5,9-diethyl-2′-hydroxy-2-methyl-6,7-benzomorphans (II, 19%, and III, 14%, respectively) and compound IV (27%) whose separation, constitutional proof, and analgetic activity are presented in this communication. De-

(1) Visiting Associate from Allahabad University, Allahabad, India.

(2) (a) J. H. Ager and E. L. May, *J. Org. Chem.*, **27**, 245 (1962); (b) J. H. Ager, S. E. Fullerton, and E. L. May, *J. Med. Chem.*, **6**, 322 (1963).

(3) J. H. Ager, S. E. Fullerton, E. M. Fry, and E. L. May, *J. Org. Chem.*, **28**, 2470 (1963), had reported that only two products, α- and β-benzomorphans were obtained in this cyclization.

SCHEME I

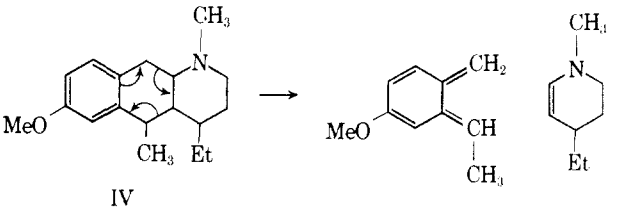


scribed also is an improved procedure for the preparation of III.

Fractional crystallization (from acetone) of the crude material obtained in the aluminum bromide cyclization of I hydrochloride in carbon disulfide gave II as the first fraction, IV of intermediate solubility, and III as the most soluble of the three products. Marked differences in the infrared spectra of III and IV in the 7–14.5-μ region (Figure 1) were helpful in the separation of these two components whose melting points and solubilities are not far apart. Cyclization of I with 85% phosphoric acid at 180° produced no IV, a 50% yield of II, and a 25% yield of III, the best yet obtained for III.

Compound IV, shown by elemental analyses to be isomeric with II and III, gave an n.m.r. spectrum indicating one $CHCH_3$ and one ethyl rather than two C-ethyl radicals. The same kind of pattern was evident in the methyl ether of IV (Figure 2) and the methine (VII), prepared by thallous hydroxide treatment of the methiodide of the methyl ether of IV, followed by dry distillation. The vinyl proton signals of VII are almost identical with those of the methines V and VI (Figure 3), derived from the α- and β-benzomorphans II and III, respectively. Thus, the quartet at 5.6–5.8 p.p.m. is clearly that of a β(to the benzene ring)-styrene proton split by the α-styrene proton and an allylic hydrogen at position 2 of the 1,2-dihydronaphthalene moiety. The doublet at 6.5–6.3 is due to the α-styrene proton. Hydrogenation of V and VII caused disappearance of these signals. The ultraviolet spectra of V and VII and their hydrogenated products were compatible with the structures shown.

The high-resolution mass spectrum of the methyl ether of IV strongly supports structure IV for the new base. The peaks at *m/e* 125 and 148 are due to a retro Diels–Alder reaction[4] of ring B.



IV

Calcd: *m/e* 148.0888 *m/e* 125.1180
Found: *m/e* 148.0896 *m/e* 125.1190

An analogous cleavage in the ethers of benzomorphans II or III would not lead to loss of the nitrogen-containing ring since it is connected through a quaternary carbon atom and the spectra lack these features.[5]

Palladium–charcoal aromatization of V and VI has been shown to give 7-methoxy-1,2-diethylnaphtha-

(4) *Cf.* xylopinone: M. Ohashi, J. M. Wilson, H. Budzikiewicz, M. Shamma, W. A. Slusarchyk, and C. Djerassi, *J. Am. Chem. Soc.*, **85**, 2807 (1963).

(5) A full report of the mass spectra of these compounds will be published elsewhere.

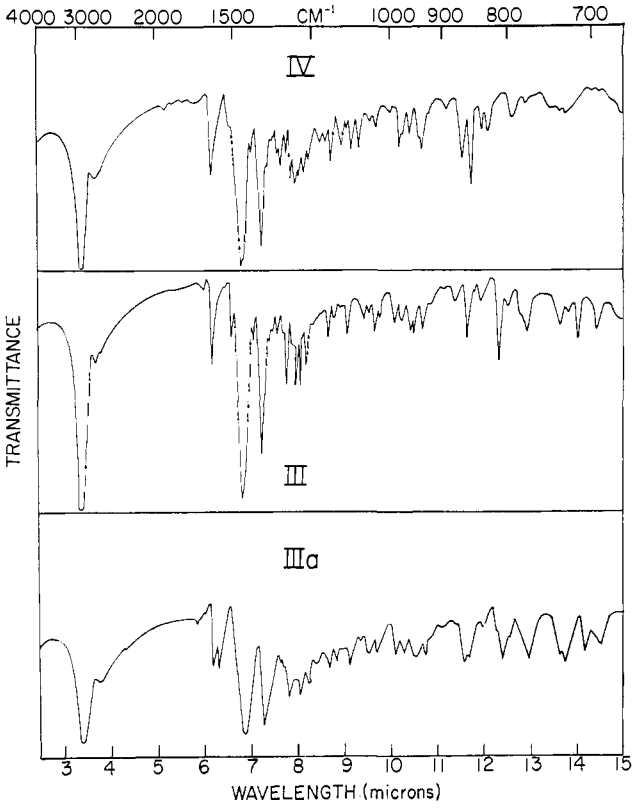


Figure 1.—Infrared spectra of III, IIIa (a second crystalline form III), and IV as Nujol mulls (Perkin-Elmer Infracord).

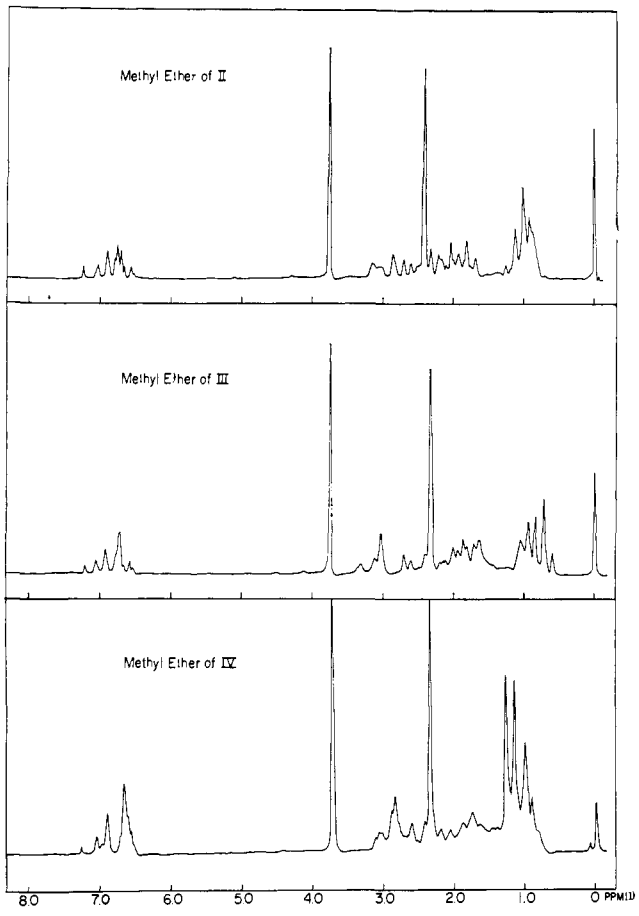


Figure 2.—Proton n.m.r. spectra of the methyl ethers of II, III, and IV in $CDCl_3$ (60 Mc., TMS reference standard).

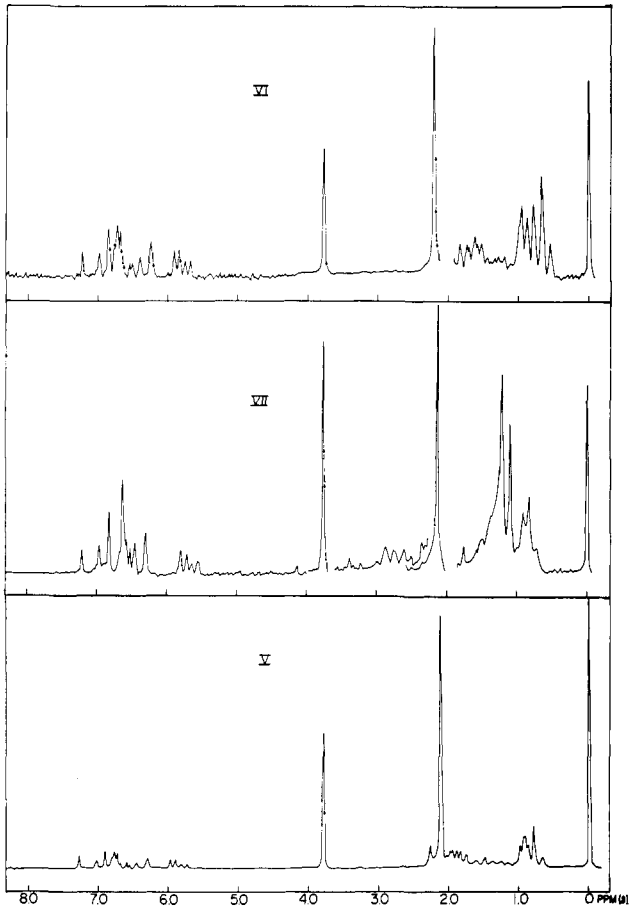
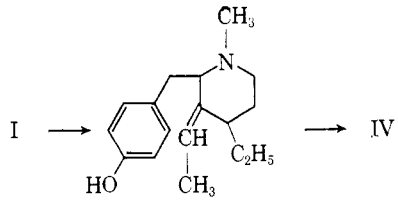


Figure 3.—Proton n.m.r. spectra of V, VI, and VII in $CDCl_3$ (60 Mc., TMS reference standard).

lene.[1a,6] Similar treatment of VII has given 7-methoxy-1-methylnaphthalene (X)[7] identical (g.l.c. and ultraviolet and n.m.r. spectra) with that synthesized from 3,4-dihydro-7-methoxy-1-methyl-2(1H)-naphthalenone (IX).[8]

To account for the formation of IV, one may assume a shift of the double bond of I to the 3-*exo* position as in XI. The stereochemistry of IV is not known but molecular models indicate that the least strained



XI

arrangement is that in which rings B and C are *trans* fused and with the methyl group equatorial and the ethyl axial. This geometry would also be consistent with a *trans* addition to the double bond of XI.

The analgetic potency of IV, about half that of the α-isomer II[2b] (between morphine and codeine), is interesting because it represents a new type of structure, an octahydrobenzo[*g*]quinoline, eliciting this

(6) S. E. Fullerton, J. H. Ager, and E. L. May, *J. Org. Chem.*, **27**, 2554 (1962).

(7) R. D. Haworth and G. Sheldrick, *J. Chem. Soc.*, 1951 (1934).

(8) J. G. Murphy, J. H. Ager, and E. L. May, *J. Org. Chem.*, **25**, 1386 (1960).

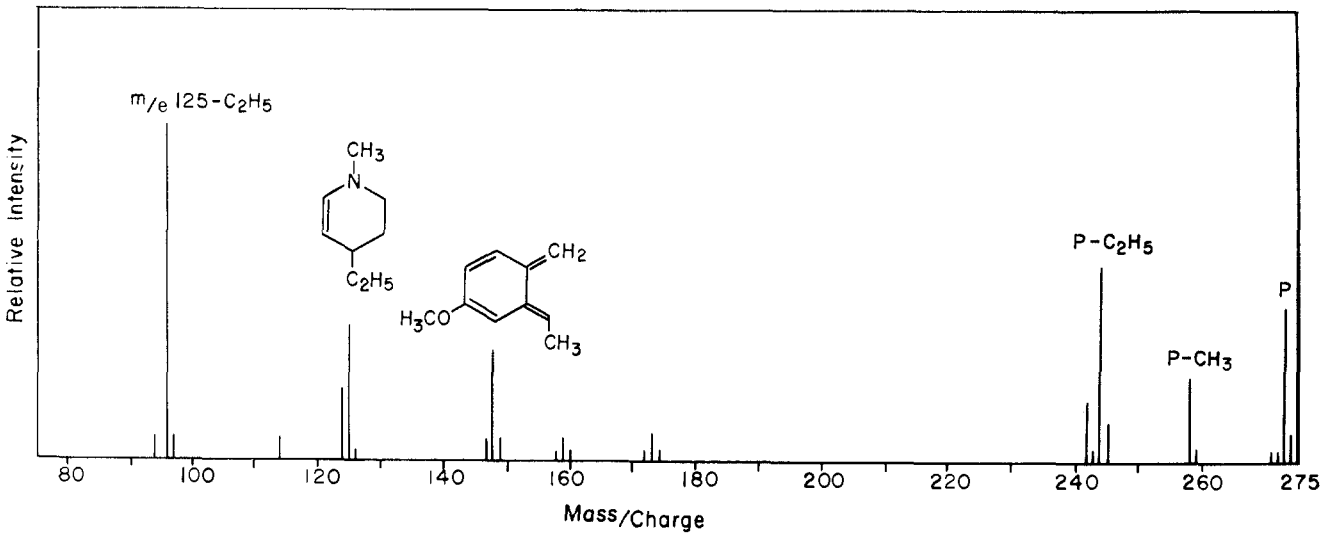


Figure 4.—Mass spectrum of IV.

behavior. Its subcutaneous acute toxicity in mice (LD_{50} 300)[2b] is fairly low so that the therapeutic index of IV is favorable.[9]

Experimental

Melting points (capillary) are corrected. Microanalyses are by the Analytical Services Section of these Institutes. Mass spectra were determined on an Associated Electronics Industries, MS-9, double-focusing mass spectrograph using an inlet temperature of 200°. Accurate mass measurements were made relative to perfluorokerosene internal standard where $C = 12.0000$. N.m.r. spectra were made on a Varian A-60 model.

1,5-Dimethyl-4-ethyl-7-hydroxy-1,2,3,4,5,10,11,12-octahydrobenzo[*g*]quinoline (IV).—To a stirred mixture of 2.4 g. of the hydrochloride of I[3] and 15 ml. of CS_2 was added 7 g. of $AlBr_3$. The mixture (protected from moisture) was stirred for 24 hr. Solvent was decanted, and the viscous residue was washed with ligroin (30–60°), then dissolved in about 200 ml. of warm water. The cooled solution was made alkaline with NH_4OH and extracted with 120–150 ml. of 3:1 butanol–benzene in four portions. The dried (Na_2SO_4) extracts were evaporated thoroughly to dryness *in vacuo*. The residue was digested with 50 ml. of boiling acetone and cooled (finally to 5°) to give 0.4 g. (19%) of II,[2a,3] m.p. 243–245°. The filtrate and washings were concentrated to 10 ml. and seeded with pure IV.[10] Cooling at room temperature for 1.5 hr. and at 0° for 1 hr. gave 0.6 g. (27%) of IV, m.p. 199–204°. The mass spectrum of IV is shown in Figure 4. It crystallized from methanol in prisms, m.p. 203–205°. The infrared spectrum is shown in Figure 1 for comparison with that of III. IV and II were quaternized by methyl iodide[11a] at essentially the same rate, ten times more rapidly than III.

Anal. Calcd. for $C_{17}H_{25}NO$: C, 78.7; H, 9.7; mol. wt., 259.3. Found: C, 78.5; H, 9.5; mol. wt., 256.9.[11b]

The filtrate and acetone washings from the 0.6 g. of IV were concentrated to 5 ml. and seeded with pure III.[2] Cooling at −5° overnight gave 0.3 g. of III, m.p. 202–204°, identified as the hydrochloride[3] and by conversion to a previously isolated[3] higher melting (213–214°) modification. The infrared patterns of these two modifications are shown in Figure 1.

(9) Compound IV has no quaternary carbon and its tertiary nitrogen is not three but four carbons removed from the aromatic ring (*cf.* E. L. May in "Medicinal Chemistry," A. Burger, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 335). Furthermore, in its most comfortable geometry IV should present a nearly planar surface to the biologic receptor site as opposed to the three-dimensional pattern of morphine and similar analgetics (*cf.* A. H. Beckett and A. F. Casy, *J. Pharm. Pharmacol.*, **6**, 986 (1954)).

(10) Seed crystals of pure IV were initially obtained from a mixture of III and IV (from the filtrate of II), separation being made *via* the hydrochloride salts. The hydrochloride of III is insoluble in acetone while that of IV is soluble and hygroscopic.

(11) (a) S. E. Fullerton, E. L. May, and E. H. Becker, *J. Org. Chem.*, **27**, 2144 (1962); (b) determined by titration with acetic–perchloric acid using oracet blue B indicator.[11b]

1,5-Dimethyl-4-ethyl-7-methoxy-1,2,3,4,5,10,11,12-octahydrobenzo[*g*]quinoline Methiodide.—Compound IV (150 mg.), 2 ml. of methanol, and 5 ml. of 3% ethereal diazomethane were stirred to solution (1–2 hr.) and left for 20 hr. During an additional 24 hr. 10 ml. more of the diazomethane was added in two portions. Solvents were evaporated, and the residue was evaporatively distilled (140–150°, 0.1 mm.) giving 148 mg. of the methyl ether of IV, λ_{max}^{EtOH} 278 mμ (ε 2139) and a shoulder at 286 mμ. In acetone it gave 195 mg. (88% over-all from IV) of methiodide, m.p. 199–200°, prisms from acetone.

Anal. Calcd. for $C_{19}H_{30}INO$: I, 30.6. Found: I, 30.7.

The hygroscopic **hydrochloride** of the **methyl ether of IV** crystallized from acetone–ether; m.p. 162–164° (froth). It was dried at 100° prior to analysis.

Anal. Calcd. for $C_{18}H_{28}ClNO$: C, 69.7; H, 9.0; Cl, 11.5; N, 4.5. Found: C, 69.3; H, 8.6; Cl, 11.9; N, 4.8.

Conversion of the Above Methiodide to VII.—The above methiodide (0.2 g.) and 2 ml. of water were kept on the steam bath while adding dropwise during 2–3 min., 5 ml. of 0.1 *M* thallous hydroxide.[12] After 20–25 min. on the steam bath, the mixture was filtered and evaporated to dryness *in vacuo*. The residue was distilled at a bath temperature of 110–120° (0.1 mm.) giving 58 mg. (42%) of **methine (VI)**, λ_{max}^{EtOH} 271 mμ (ε 14,500) (for n.m.r. spectrum, see Figure 3).

Hydrogenation of 50 mg. of the methine VI in alcohol with 10 mg. of platinum oxide and distillation of the product (150°, 0.1 mm.) yielded **2-(3-dimethylamino-1-ethylpropyl)-7-methoxy-1-methyl-1,2,3,4-tetrahydronaphthalene** whose **hydrobromide** (from ethereal HBr) crystallized from acetone–ether in fine needles of m.p. 166–169°.

Anal. Calcd. for $C_{19}H_{32}BrNO$: C, 61.6; H, 8.7. Found: C, 61.8; H, 8.7.

Degradation of the Methiodide of II Methyl Ether.—The methiodide of the methyl ether of II[3a] (0.4 g.) and 5 ml. of 10% NaOH were refluxed gently for 1–2 hr. Extraction with ether and drying (Na_2SO_4) and evaporation of the ether left 0.2 g. (71%) of V,[13] λ_{max}^{EtOH} 273 mμ (ε 12,000) (for n.m.r. spectrum, see Figure 3). It was dissolved in ethanol and hydrogenated in the presence of platinum oxide. The resultant **1-(2-dimethylaminoethyl)-1,2-diethyl-7-methoxy-1,2,3,4-tetrahydronaphthalene**, λ_{max}^{EtOH} 281, 288 (sh) mμ (ε 3800, 3300), was converted to the **hydrochloride** with ethereal HCl; yield 0.15 g., m.p. 150–154°, plates from acetone–ether.

Anal. Calcd. for $C_{19}H_{32}ClNO$: C, 70.0; H, 9.9. Found: C, 70.3; H, 10.2.

(12) In contrast to the methyl ethers of II, III, and similar tetrahydronaphthalene and tetrahydrophenanthrene structures [see ref. 2a and E. L. May and E. M. Fry, *J. Org. Chem.*, **22**, 1366 (1957)], with benzylic hydrogens β to the nitrogen, the methiodide of the methyl ether of IV would not undergo Hofmann cleavage with aqueous alkali. When 10% NaOH at 100° was used, methiodide was recovered. With 30% NaOH at 100° a quantitative elimination of methyl iodide and recovery of the methyl ether of IV were observed.

(13) Palladium–charcoal aromatization of V gave 1,2-diethyl-7-methoxynaphthalene.[2a]

Similarly, the methiodide of the methyl ether of III gave VI whose n.m.r. spectrum is shown in Figure 3.

7-Methoxy-1-methylnaphthalene.[7] **A. From IX.**—Compound IX (3 g.) in 25 ml. of alcohol was treated with 1–2 g. of $NaBH_4$. After gas evolution had ceased, aqueous NaOH was added, and the mixture was extracted with ether. Evaporative distillation (150°, 0.1 mm.) of the residue from drying and evaporation of the ether gave 2.5 g. of the **2-carbinol** corresponding to IX (C, H analysis correct), retention time[14] 5 min. at 148°. This carbinol (0.5 g.) and 0.5 g. of 10% palladium–charcoal were kept at 300–315° for 30 min. to give 20% yield of hydrocarbon which was purified through its picrate, m.p. 110–114°. The free hydrocarbon X, m.p. 43–45° from ligroin (30–60°), had a retention time[14] of 2 min. at 145° whose n.m.r. pattern ($CDCl_3$), TMS reference standard, showed 6 protons in the 6.9–7.9-p.p.m. region, 3 methoxy protons at 3.95 p.p.m. and 3 C-methyl protons at 2.6 p.p.m.; λ_{max}^{EtOH} 332, 317, 288, 277, 266, 232 mμ (ε 1800, 1360, 3400, 4200. 2450, 105,000).

B. From VII.—Similar aromatization of 0.3 g. of VII with 0.2 g. of 10% palladium–charcoal gave a mixture from which a fraction could be isolated with physical properties identical with those given above for authentic X.

Cyclization of I with 85% Phosphoric Acid.—The hydrochloride[3] of the methyl ether of I (10 g.) and 50 ml. of 48% HBr were refluxed for 20 min., cooled, and made alkaline with NH_4OH. Three extractions with $CHCl_3$ and evaporation of the extracts left 9.0 g. of crude I, which with 40 ml. of 85% H_3PO_4 was kept at 185–190° (bath temperature) for 35 hr. The cooled solution was made basic with NH_4OH and extracted four times with a total of 250 ml. of $CHCl_3$. Drying and evaporation of the $CHCl_3$ left 7.8 g. of solid which was digested for 10 min. with 200 ml. of boiling acetone while the volume decreased to 175 ml. The mixture was cooled to −15° during 2 hr. to give 4.9 g. of II,[2a,3] m.p. 240–245°. The filtrate was evaporated to dryness and the residue evaporatively distilled (0.05 mm.). The 2.4 g. of semisolid was digested with boiling acetone (final volume 5–7 ml.). Cooling to −15° gave 2.2 g. of III,[2a,3] m.p. 195–205° identified by its infrared spectrum (Figure 1) and hydrochloride salt. Occasionally, another crystalline modification separated whose infrared spectrum was that shown by IIIa, Figure 1. The two were interconvertible and gave the same HCl salt.[2a,3]

(14) Research Specialties gas chromatograph, 6-ft. coiled glass column, SE 30, Chromosorb W (60–80 mesh).

Structures Related to Morphine. XXXI.[1] 2′-Substituted Benzomorphans

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Received May 5, 1965

Several 2′-nitro-, 2′-amino-, and 2′-halo-α- and -β-5,9-dialkyl-2-methyl-6,7-benzomorphans have been synthesized. In general these compounds are less potent as analgetics and more acutely toxic than corresponding 2′-H or 2′-OH derivatives. Comparable substitution in the morphine and morphinan series has not been reported. New analgetic ED_{50} values for Caesarian-Derived General Purpose mice are given; they are approximately half those obtained with previously used General Purpose mice which were kept under less sanitary conditions.

The 2′-hydroxy group[2] in various benzomorphans and related compounds has been found to enhance analgetic potency and reduce toxicity when compared with their 2′-H analogs.[3] To our knowledge, compounds with substituents other than hydroxyl, or derivatives thereof, in the comparable position in the benzomorphans, morphine, or the morphinans have not been examined. It seemed of interest, as part of our program on the role of the substituent in analgetic effect, to prepare 6,7-benzomorphans having nitro, fluoro, chloro, and amino as the 2′-substituent.

The 2′-nitro compounds (II, Va, and Vb) were prepared by nitration of the known α- and β-5,9-diethyl-2-methyl-6,7-benzomorphan (I and IVa)[3] and β-2,5,9-trimethyl-6,7-benzomorphan (IVb),[4] respectively; amino analogs (III and VI) were obtained by catalytic reduction of the corresponding nitro compounds (see Chart I). The 2′-chloro (Xa) and 2′-fluoro (Xb) compounds could be obtained best *via* total synthesis by the Grewe[5] method. An alternative procedure for Xa based on the Stevens rearrangement[6] of 1-*p*-chlorobenzyl-1,3,4-trimethyl-1,2,5,6-tetrahydropyridinium chloride gave IXa in low yield along with two isomeric products whose structures are being investigated.

The cyclization of IXa to Xa could be readily effected with hot HBr, while IXb and this reagent gave poor yields of Xb. Hot phosphoric acid was effective in cyclizing IXb, although a troublesome by-product was formed simultaneously. Pure Xb could be obtained, ultimately, only by use of preparative thin layer chromatography.

For proof of structure, Xa and Xb were degraded to 1,2-dimethylnaphthalene (XIIIa) and 7-fluoro-1,2-dimethylnaphthalene (XIIIb), which were purified through their picrates.[5] The constitution of XIIIb rests upon its elemental and spectral analyses. Ultraviolet and n.m.r. spectra indicated the naphthalene nucleus, and the n.m.r. spectrum showed the presence of two methyl groups on an aromatic nucleus (2.48 and 2.52 p.p.m.) and a complex pattern for the five protons in the aromatic region, centered at 7.5 p.p.m. The combined data are clearly consistent with the structure XIIIb. Elemental analysis of the picrate of the product obtained by palladium-on-charcoal aromatization of XIIa showed the, perhaps not unexpected, loss of chlorine. The physical properties of this picrate were identical with the known 1,2-dimethylnaphthalene picrate. The n.m.r. spectrum of XIIIa was similar to XIIIb, having the two methyl groups at 2.45 and

(1) Paper XXX: B. C. Joshi, C. F. Chignell, and E. L. May, *J. Med. Chem.*, **8**, 694 (1965).

(2) The 2′-position in benzomorphan compounds is comparable to the 3-position in morphine and the morphinans.

(3) A. E. Jacobson and E. L. May, *J. Med. Chem.*, **7**, 409 (1964); see ref. 2 therein.

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