IV is insoluble in water but soluble in ether and alcohol. It is optically inactive both in organic solvents and in sodium hydroxide solution (as sodium salt).

The infrared absorption spectrum of compound IV does not show the band ($cm.^{-1}$) at 3250 (bonded OH).

Aromatization of III. A mixture of III (200 mg.) and 50 mg. of sulfur was heated in a small porcelain dish covered with a bigger one which contained ice water. The small dish was heated in a paraffin bath for 0.5 hr. at 180–250°. A strong odor of hydrogen sulfide was discernable immediately after the beginning of the heating. The production of hydrogen sulfide could be confirmed by lead acetate paper. From the small dish a substance sublimed and deposited as yellow crystals on the bottom of the big cooling dish. The crystals were dissolved in a solution of sodium hydroxide and reprecipitated by acidifying with hydrochloric acid. They could be extracted by ether, regained on evaporation of the solvent, and recrystallized from boiling water (compound VI); m.p. 112°.

Anal. Calcd. for $C_8H_{16}O_2$: C, 72.00; H, 6.66; mol. wt., 150. Found: C, 71.1; H, 6.78; mol. wt., 153 (titration with 0.1*N* sodium hydroxide).

VI is soluble in sodium carbonate or sodium bicarbonate solutions with the evolution of carbon dioxide; it is insoluble in cold water. Reactions with alkaline potassium permanganate or sodium nitroprusside solutions were negative. Methanolic, ethanolic or ether solutions of VI do not show any optical activity.

The amide of VI. A mixture of VI (18 mg.) with a few drops of twice redistilled thionyl chloride was heated at reflux for 30 min. at 70°. The excess thionyl chloride was distilled and 3 ml. of concd. ammonia was added to the residue which was again heated for several minutes. On cooling a crystalline precipitate appeared which could be filtered and recrystallized from 50% alcohol; m.p. 140°.

Anal. Calcd. for $C_9H_{11}ON$: C, 74.48; H, 7.58; N, 9.65. Found: C, 74.16; H, 7.03; N, 9.84.

By the analysis and m.p. of VI and of its amide, VI is identified as 2,6-dimethylbenzoic acid.[22, 23]

Ozonolysis of III. Compound III (50 mg.) was dissolved in a mixture of 10 ml. of glacial acetic acid and 3 ml. of acetic anhydride (for prevention of solidification of the acetic acid in the cold) in a small flask and immersed in an ice water bath. An ozone-oxygen mixture (1:10) from an ozonizer was passed through the solution. Zinc powder, 30 mg., was added and the mixture heated for 1 hr. on a boiling water-bath. The zinc was eliminated by filtration and the acetic acid and acetic anhydride by distilling *in vacuo*. The sirupy residue could not be crystallized, but it reduced Fehling's solution and gave positive nitroprusside and iodoform reactions. Iodoform crystals, m.p. 119°, could be isolated and gave an unchanged melting point after mixing with authentic iodoform.

Enzymatic hydrolysis of oleuropein. The oleuropein is attacked neither by emulsin which was very active in control experiments with amygdalin and salicin, nor by a preparation of α-glucosidase from baker yeast which was active in control experiments with maltose, nor by a lipase which was active on olive oil. Tannase, which was prepared from *Aspergillus niger* according to Freudenberg and Vollbrecht,[14] showed activity towards oleuropein at a temperature of 35° at *p*H 5. Evidence of hydrolysis was the liberation of protocatechuic acid which could be extracted and determined quantitatively by titration with sodium hydroxide solution (0.1*N*) against phenolphthalein. The amount of protocatechuic acid did not exceed 10% of the calculated amount for the total hydrolysis of oleuropein. No free oleuropeic acid could be detected in the hydrolyzate.

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(22) A. Shouberg and O. Kramer, *Ber.*, **55**, 1189 (1921).

(23) E. H. Rodd, *Chemistry of Carbon Compounds*, Vol. III, Part A, p. 544, Elsevier, New York (1954).

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF ARTHRITIS AND METABOLIC DISEASES, NATIONAL INSTITUTES OF HEALTH, PUBLIC HEALTH SERVICE, DEPARTMENT OF HEALTH, EDUCATION AND WELFARE]

Structures Related to Morphine. XVI.[1] Stereochemical Control of Addition of Hydrogen to 9-Oxobenzomorphans

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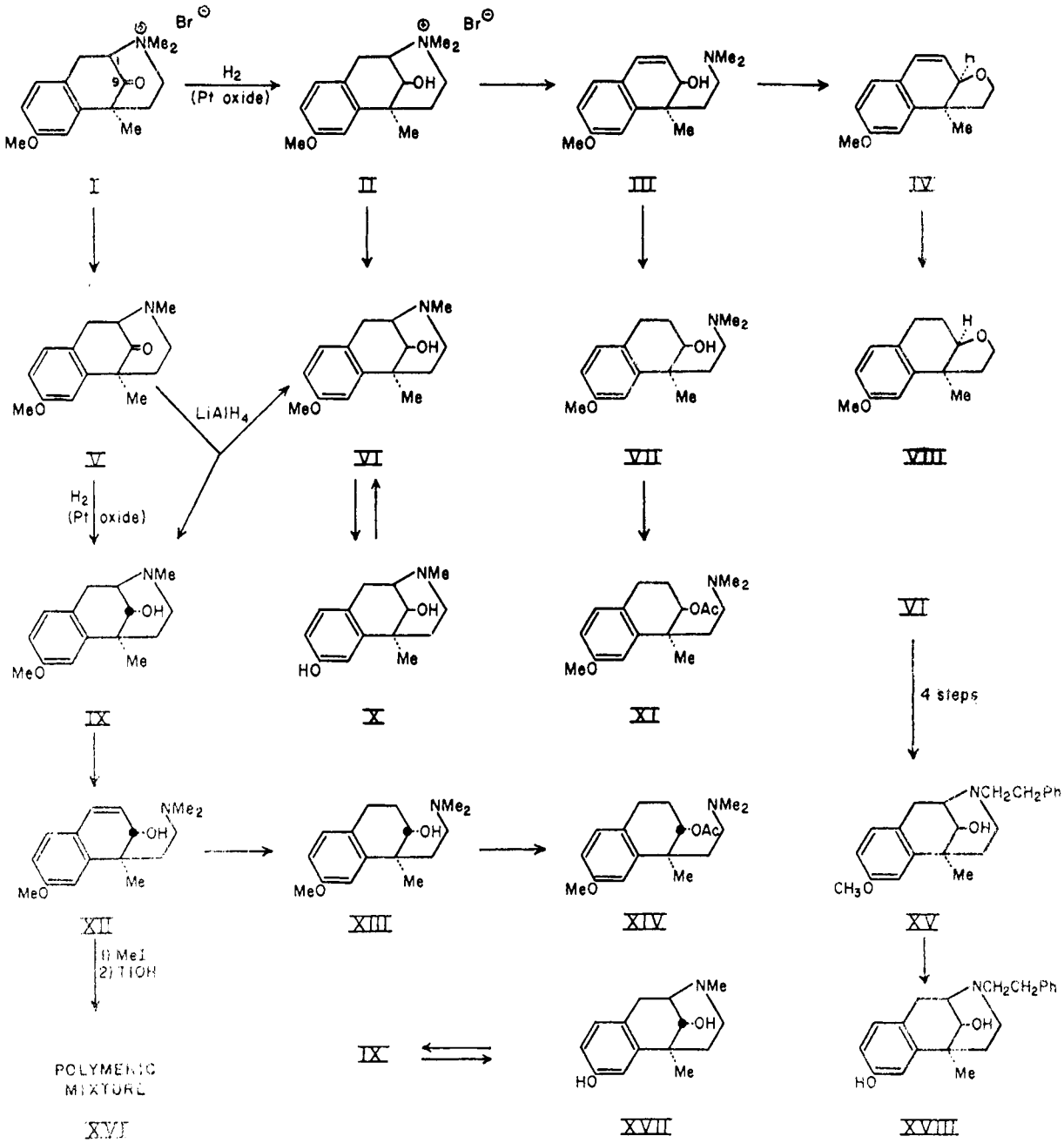
Received July 15, 1960

Hydrogenation of 2′-methoxy-2,5-dimethyl-9-oxo-6,7-benzomorphan methobromide (I) with platinum oxide has produced the carbinol methobromide II with the hydroxyl group oriented toward the nitrogen of the *cis*-fused *N*-containing ring as shown by infrared analysis and by its conversion to the *cis*-tetrahydrofurano compounds IV and VIII. Pyrolysis of II in boiling 1-nonanol gave the free base (VI). Similar hydrogenation of the base V yielded the diastereoisomeric carbinol (IX) to the apparent exclusion of VI; lithium aluminum hydride reduction of V afforded a 50–60% yield of IX and a 10% yield of VI. Treatment of VI and IX with boiling 48% hydrobromic acid led to the phenolic compounds X and XVII, respectively. Compound VI was also converted to the phenethyl analogs XV and XVIII which along with VI, IX, X, the di-*O*-acetyl derivative of X, and XVIII have been tested in mice for analgesic potential.

In the preceding paper[1] we reported that methylmagnesium iodide adds to 2′-methoxy-2,5-dimethyl-9-oxo-6,7-benzomorphan methiodide (I) to give a 9-methylcarbinol with the hydroxyl oriented toward the nitrogen (equatorial for the hydroaromatic ring), while the free base (V) and methyllithium or methylmagnesium iodide give principally the diastereoisomer. The present report is concerned with the addition of hydrogen to I and V to further study this perhaps partially electrically controlled asymmetric induction and to prepare compounds of possible neuropharmacologic value.

Hydrogenation of I using platinum oxide afforded the carbinol II with the hydroxyl *cis* to the iminoethano system analogous to the Grignard reaction.[1] This was proved by conversion of II in good yield to the furano compounds IV and VIII and by the fact that the infrared spectrum of the base VI, derived from II indicated strong OH—N bonding

(1) E. L. May and Hiroshi Kugita, *J. Org. Chem.*, **26**, 188 (1961).



(broad band at 3495 cm.$^{-1}$) irrespective of concentration.[1]

Similar hydrogenation of the base V gave exclusively the opposite configuration at C-9 (compound IX) again in analogy with the reaction of methyllithium with V.[1] Addition of hydrogen to V with lithium aluminum hydride gave about 50% of IX and 10% of VI.[2] The infrared spectrum of IX showed two peaks in the hydroxyl region, one at 3634 cm.$^{-1}$ (free OH) and a stronger one at 3591 cm.$^{-1}$ (OH—π bonding).[1] Again these maxima were independent of dilution. Attempts to convert IX to the *trans*-fused tetrahydrofurano compound[1] gave a nitrogen-free product which rapidly polymerized and whose ultraviolet maximum (277 mμ) showed a marked, rapid hypsochromic shift in alcohol. Initially its infrared spectrum gave some

(2) The high stereospecificity of these reductions and analogy with the addition of methyl-metallo reagents to II and V would appear to support our postulate[1] that when the entering groups are small the charge on the nitrogen is of major importance in stereochemical control. In the reaction of either ethyl- or propylmagnesium iodide with II, no C-alkylation was noted but in each instance a small yield of methiodide could be obtained which, after pyrolysis in 1-nonanol, gave the reduction product VI as the sole product [*cf.* F. E. Royals, *Advanced Organic Chemistry*, Prentice-Hall, New York, 1954, p. 687, and E. L. May and T. D. Perrine, *J. Org. Chem.*, 18, 1572 (1953)]. Ethylmagnesium iodide and the base V, on the other hand, gave a 40% yield of the β-ethylcarbinol and little or none of the α-isomer.

indication of the presence of a free hydroxyl and a vinyl group and some bands characteristic of a tetrahydrofuran.[3]

Hydrogenation of III and XII with palladium-charcoal yielded the tetrahydronaphthalene carbinols VII and XIII respectively whose *O*-acetyl derivatives (XI and XIV) showed no appreciable infrared spectral differences either as a liquid film or in carbon disulfide in the 1240 cm.$^{-1}$ region. The axial acetate of 1-methyl-2,6-diphenyl-4-piperidinol, on the other hand, presents a more complicated pattern in the 1220–1250 cm.$^{-1}$ region than the equatorial which exhibits a single maximum.[4]

An attempt to convert VI to IX by equilibration with aluminum isopropoxide in refluxing isopropyl alcohol[5] (seventy hours) gave an 85% recovery of VI. There was no evidence of inversion.

Conversion of VI and IX to the corresponding phenolic compounds X and XVII was effected by boiling 48% hydrobromic acid without rearrangement or inversion at C-9 as shown by diazomethane methylation of X and XVII to VI and IX respectively. Compound VI was also transformed into the phenethyl analogs XV and XVIII by standard reactions.[6] These six carbinols and the di-*O*-acetyl derivative of X have been evaluated[7] in mice for analgesic potential. Only XVIII and the di-*O*-acetyl derivative of X, both at least twice as potent as morphine, showed promise. In general the 9-carbinols were less effective than the 9-methyl relatives.[1]

EXPERIMENTAL

Melting points were determined in a capillary (Hershberg apparatus, total-immersion thermometers). Microanalyses were done by Paula Parisius, Evelyn Peake, and Byron Baer of the service analytical laboratory. Infrared spectra are by H. K. Miller and Ann Wright of this Institute, unless otherwise noted.

α-9-Hydroxy-2'-methoxy-2,5-dimethyl-6,7-benzomorphan methobromide (II).[8] Platinum oxide (0.2 g.), 2.0 g. of I[9] and 40 ml. of methanol absorbed one molar equivalent of hydrogen during 1 hr. The filtered solution was evaporated to dryness at the water pump. Digestion of the residue with 30 ml. of acetone, cooling and filtration, gave a precipitate which was recrystallized from ethanol; yield 1.5 g. (75%), m.p. 234–236°, λ_{max}^{Nujol} 3.11 μ.

Anal. Calcd. for $C_{16}H_{24}BrNO_2$: C, 56.13; H, 7.06; Br, 23.35. Found: C, 55.92; H, 6.94; Br, 23.21.

α-9-Hydroxy-2'-methoxy-2,5-dimethyl-6,7-benzomorphan (VI) *hydrobromide*. II (1.5 g.) and 9 ml. of 1-nonanol were refluxed (stirring) for 15 min. (clear solution after 10 min.) cooled under nitrogen and diluted with ether. The mixture was extracted thrice with dilute hydrochloric acid. The combined extracts were made alkaline and extracted with ether. Drying and evaporation of these extracts left an oil which was distilled evaporatively (bath temperature 140–150°/0.2 mm.) to give 0.6 g. (60%) of VI which in 5 ml. of acetone was neutralized with 30% hydrogen bromide in acetic acid. The hydrobromide resulting (0.7 g.) melted at 204–207°; needles from ethanol-ethyl acetate, m.p. 214–216°, λ_{max}^{Nujol} 3.1 μ.

Anal. Calcd. for $C_{15}H_{22}BrNO_2$: C, 54.88; H, 6.75; Br, 24.34. Found: C, 54.85; H, 6.96; Br, 24.30.

The *base* VI[10] crystallized from petroleum ether (b.p. 30–60°) in granules of m.p. 81–82° $\lambda_{max}^{CHCl_3}$ 2.87 μ, λ_{max}^{Nujol} 2.95 μ, $\nu_{max}^{CCl_4}$ 3495 cm.$^{-1}$ (broad, indicative of intramolecular OH–N bonding).[11]

α-2',9-Dihydroxy-2,5-dimethyl-6,7-benzomorphan (X). The hydrobromide of VI (0.7 g.) and 5 ml. of 48% hydrobromic acid were refluxed for 15 min., cooled, made alkaline with ammonium hydroxide and extracted four times with a total of 30 ml. of chloroform. The dried (sodium sulfate) extracts were evaporated to dryness. The residue, in ether, was treated with 30% hydrogen bromide in acetic acid to give the hydrobromide of X which crystallized from ethanol-ethyl acetate in a yield of 0.3 g. (45%), m.p. 223–225°. It was converted to the base (aqueous ammonium hydroxide) which crystallized from ether-ligroin (b.p. 30–60°) in rectangles, m.p. 155–157°.

Anal. Calcd. for $C_{14}H_{19}O_2$: C, 72.08; H, 8.19. Found: C, 71.93; H, 8.21.

β-9-Hydroxy-2'-methoxy-2,5-dimethyl-6,7-benzomorphan (IX). Methanol (8 ml.), 0.48 g. of V[9] and 0.1 g. of platinum oxide absorbed one molar equivalent of hydrogen during 80 min. The filtered solution was evaporated to dryness *in vacuo*. Distillation of the residue at 165–175° (air-bath temperature)/0.3 mm. gave 0.46 g. of product which crystallized from ether-ligroin (b.p. 30–60°) in needles of m.p. 115.5–117°; $\lambda_{max}^{CHCl_3}$ 2.77 (weak, sharp) and 2.9 μ, $\nu_{max}^{CCl_4}$ 3634 cm.$^{-1}$ (medium) and 3591 cm.$^{-1}$ (stronger).[11] These maxima were independent of dilution.

Anal. Calcd. for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.55. Found: C, 72.86; H, 8.34.

The *picrate* crystallized from ethanol in yellow needles of m.p. 213–214° dec., λ_{max}^{Nujol} 2.85 (sharp) and 2.98 μ.

Anal. Calcd. for $C_{21}H_{24}N_4O_9$: C, 52.93; H, 5.07. Found: C, 53.04; H, 4.79.

The *hydrochloride* crystallized from ethanol-ethyl acetate in needles, m.p. 243–245°, λ_{max}^{Nujol} 3.05 μ.

Anal. Calcd. for $C_{15}H_{22}ClNO_2$: C, 63.48; H, 7.79; Cl, 12.49. Found: C, 63.33; H, 7.72; Cl, 12.24.

The *methiodide* crystallized from ethanol-acetone in rectangles, m.p. 203–205°, λ_{max}^{Nujol} 3.07 μ.

Anal. Calcd. for $C_{16}H_{24}INO_2$: C, 49.35; H, 6.21. Found: C, 49.57; H, 6.29.

Reduction of V with lithium aluminum hydride. To a solution of 0.1 g. of lithium aluminum hydride in 20 ml. of dry ether was added 0.66 g. of V in 10 ml. of dry ether. After refluxing for 2 hr. 0.4 ml. of water was added and inorganic material was filtered. The filtrate was concentrated somewhat, cooled and filtered to give 0.23 g. of IX (β-isomer), m.p. 108–110°. The filtrate was evaporated to dryness and the residue, in 3 ml. of acetone, was treated with dry hydrogen chloride to a *p*H of 6. Cooling gave 0.11 g. of the hydrochloride of IX (total yield of β-isomer 49%), m.p. 230–232° after a recrystallization from ethanol-ethyl acetate. The

(3) L. J. Bellamy, *Infrared Spectra of Complex Molecules*, Wiley, New York, 1954, p. 104.

(4) R. E. Lyle and G. G. Lyle, *J. Org. Chem.*, **24**, 1679 (1959).

(5) A. A. Youssef, M. E. Baum, and H. H. Walborsky, *J. Am. Chem. Soc.*, **81**, 4709 (1959).

(6) E. L. May and N. B. Eddy, *J. Org. Chem.*, **24**, 1435 (1959).

(7) N. B. Eddy, chief of the section on analgesics of this Institute.

(8) The α and β designations are arbitrary (*cf.* ref. 1).

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

(10) Refluxing 0.37 g. of VI and 0.4 g. of aluminum isopropoxide, in isopropyl alcohol containing 0.2 ml. of acetone for 70 hr.[5] resulted in no inversion of the hydroxyl group and recovery of 0.33 g. of VI.

(11) We acknowledge the advice and aid of Dr. H. M. Fales of the National Heart Institute, in this determination, made in the Beckmann IR-7.

acetone filtrate was evaporated to dryness and the residue converted to the base (dilute ammonium hydroxide-ether). Evaporation of the ether layer left crude VI which gave 0.1 g. (11.3%) of the hydrobromide of VI (α isomer); m.p. 213–216°.

β-2′,9-Dihydroxy-2,5-dimethyl-6,7-benzomorphan (XVII) *hydrobromide.* The hydrochloride of IX (0.4 g.) and 4 ml. of 48% hydrobromic acid were refluxed gently for 10 min. and evaporated to dryness at the water pump. The residue was washed thrice with ether and triturated with acetone to give 0.3 g. (70%) of crystalline hydrobromide; m.p. 230–232° dec. after a recrystallization from ethanol-ethyl acetate.

Anal. Calcd. for $C_{14}H_{20}BrNO_2$: C, 53.51; H, 6.41. Found: C, 53.54; H, 6.65.

The base (XVII) crystallized from ethyl acetate in needles of m.p. 215–217°.

Anal. Calcd. for $C_{14}H_{19}NO_2$: C, 72.08; H, 8.19; N, 6.00. Found: C, 71.40; H, 8.34; N, 5.84.

Methylation of X and XVII with ethereal diazomethane (ethanol, 2 days, room temperature) gave VI and IX respectively, showing no inversion at C_9 or rearrangement during the acid *o*-demethylation.

α-2′,9-Diacetoxy-2,5-dimethyl-6,7-benzomorphan hydrobromide. V (0.47 g.) and 4 ml. of acetic anhydride were refluxed for 1.5 hr., treated with water and made alkaline with ammonium hydroxide. The base was extracted with chloroform and distilled at 160–170° (bath temperature)/0.3 mm. to give a viscous oil which, in acetone, was neutralized with 30% hydrogen bromide in acetic acid giving 0.58 g. of hydrobromide, m.p. 252–254°. Recrystallized from 95% ethanol, the m.p. rose to 263–264° rectangles.

Anal. Calcd. for $C_{18}H_{24}BrNO_4$: C, 54.29; H, 6.07. Found: C, 54.53; H, 5.80.

α-9-Hydroxy-2′-methoxy-5-methyl-2-phenethyl-6,7-benzomorphan (XV) *hydrobromide.* By a procedure described for the corresponding 9-methyl carbinol[1] this hydrobromide was obtained (from 0.8 g. of VI) in a yield of 0.2 g. (0.4 g. of VI was recovered after the phenylacetylation step), m.p. 233–235° after a recrystallization from acetone-ethanol.

Anal. Calcd. for $C_{22}H_{28}BrNO_2$: C, 63.16; H, 6.74. Found: C, 62.92; H, 6.98.

α-2′,9-Dihydroxy-5-methyl-2-phenethyl-6,7-benzomorphan (XVIII) *hydrobromide.* The hydrobromide of XV (0.2 g.) and 3 ml. of 48% hydrobromic acid was refluxed for 10 min. and evaporated to dryness at the water pump. Ethanol was added and the evaporation repeated. The residue was washed with ether several times and triturated with acetone giving 0.12 g. of XVIII hydrobromide, m.p. 194–195° after recrystallization from ethanol.

Anal. Calcd. for $C_{21}H_{26}BrNO_2 \cdot {}^1/_2\ C_2H_5OH$: C, 61.82; H, 6.83. Found: C, 61.57; H, 6.67.

The *hydrochloride* melted at 214–216° after recrystallizing from ethanol and drying at 100° for 3 hr.

Anal. Calcd. for $C_{21}H_{26}ClNO_2$: C, 70.09; H, 7.28. Found: C, 70.19; H, 7.55.

α-1,2-Dihydro-2-hydroxy-7-methoxy-1-methyl-1-(2-dimethylaminoethyl) naphthalene (III). II (0.5 g.) and 7 ml. of 10% sodium hydroxide were refluxed gently for 10 min. The liberated oil was dried (sodium sulfate) in ether. Evaporation of the ether left a residue which crystallized from petroleum ether (b.p. 30–60°) in rectangles (0.23 g. 66%) of m.p. 66–68°, $\lambda_{max}^{C_2H_5OH}$ 274 mμ (ε 12,670), $\lambda_{max}^{CHCl_3}$ 3.0 μ (broad) λ_{max}^{Nujol} 3.25 μ (broad).

Anal. Calcd. for $C_{16}H_{23}NO_2$: C, 73.51; H, 8.86. Found: C, 73.23; H, 8.59.

1,2,3a,4,5,9b-Hexahydro-8-methoxy-9b-methylnaphthol(2,1-b)furan (cis) (VIII). III (220 mg.), 140 mg. of methyl iodide, and 3 ml. of methanol were refluxed for 1 hr. to give, from ethanol, 300 mg. of the methiodide, m.p. 182–184° dec., λ_{max}^{Nujol} 2.94 μ. (*Anal.* Calcd. for $C_{17}H_{26}INO_2$: C, 50.62; H, 6.49. Found: C, 50.67; H, 6.57). This methiodide (280 mg.), 3 ml. of water and 3.1. ml. of 0.23*M* thallous hydroxide were kept on the steam bath for 10 min. and filtered from thallous iodide. The filtrate was evaporated to dryness *in vacuo* and the residual methohydroxide of III distilled at 105–115° (0.3 mm.) giving 160 mg. of colorless distillate which, in ether, was washed with 5% hydrochloric acid, then water, dried and redistilled; yield of IV[12] 130 mg. (87%), $\lambda_{max}^{C_2H_5OH}$ 272 mμ (ε 14,730), $\lambda_{max}^{CHCl_3}$ 9.3 μ.[3] Freshly prepared IV (90 mg. in a little methanol) was added to 20 mg. of pre-reduced platinum oxide in 3 ml. of methanol and the mixture shaken under hydrogen until absorption ceased: one molar equivalent was absorbed. The reduction product was distilled at 0.3 mm. (bath temperature 95–105°), giving 85 mg. of VIII, $\lambda_{max}^{C_2H_5OH}$ 280 mμ (ε 2410), $\lambda_{max}^{CHCl_3}$ 9.31 μ.

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.71; H, 8.52.

α-2-Hydroxy-7-methoxy-1-methyl-1-(2-dimethylaminoethyl)-1,2,3,4-tetrahydronaphthalene VII *hydrochloride.* III (340 mg.), 0.3 g. of 5% palladium-charcoal, and 15 ml. of methanol absorbed one molar equivalent of hydrogen during 20 min. The filtered solution was evaporated to dryness at the water pump leaving a residue which, in acetone, was neutralized with dry hydrogen chloride and left overnight at −5°. The hydrochloride which crystallized (285 mg.) melted at 177–180°; λ_{max}^{Nujol} 2.84, 3.04 μ.

Anal. Calcd. for $C_{16}H_{26}ClNO_2$: C, 64.07; H, 8.73; Cl, 11.82. Found: C, 63.69; H, 9.02; Cl, 11.66.

The *O-acetyl derivative* (XI), λ_{max}^{smear} 5.74, 8.06 μ, was analyzed as the *picrate;* m.p. 142–143° (from alcohol).

Anal. Calcd. for $C_{24}H_{30}N_4O_{10}$: C, 53.92; H, 5.65. Found: C, 53.83; H, 5.83.

β-2-Hydroxy-7-methoxy-1-methyl-1-(2-dimethylaminoethyl)-1,2,3,4-tetrahydronaphthalene (XIII) *hydrochloride.* The methiodide of IX (0.47 g.) and 5 ml. of 10% sodium hydroxide were refluxed gently for 15 min. The separated oil (XII) was dried in ether and distilled at 0.3 mm. (140–155°, bath temperature) yielding 230 mg. of colorless XII,[13] $\lambda_{max}^{C_2H_5OH}$ 275 mμ (ε 12,680), $\lambda_{max}^{CHCl_3}$ 2.8, 3.0 μ. XII (30 mg.) was hydrogenated as described for III giving 25 mg. of the hydrochloride of XIII, rectangles from ethanol-ethyl acetate, m.p. 206–208°, λ_{max}^{Nujol} 2.94 μ.

Anal. Calcd. for $C_{16}H_{26}ClNO_2$: C, 64.06; H, 8.73. Found: C, 63.52; H, 8.47.

The *O-acetyl derivative* (XIV), λ_{max}^{smear} 5.74, 8.05 μ, crystallized as the *hydrobromide* (from acetone); m.p. 200–202°, λ_{max}^{Nujol} 5.75 μ.

Anal. Calcd. for $C_{18}H_{28}BrNO_3$: C, 55.96; H, 7.30. Found: C, 56.18; H, 7.34.

Reaction of I with ethylmagnesium bromide. The reaction was carried out as with methylmagnesium iodide and I.[1] From 1.5 g. of I, the yield of crude methiodide (containing inorganic salts) was 0.8 g. This was pyrolyzed in 1-nonanol as described for II giving 0.25 g. of distilled base, $\lambda_{max}^{CHCl_3}$ 2.9 μ, the hydrobromide and picrate of which were found to be identical with those of VI obtained by catalytic hydrogenation of I and pyrolysis of the carbinol (II) thus formed. Substantially the same results were obtained with propylmagnesium iodide and I.[2]

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(12) Because of the apparent air sensitivity of this compound it was difficult to get meaningful C, H, values for IV.

(13) Exhaustive methylation of XII as described for III gave nitrogen-free material which rapidly polymerized. The initial $\lambda_{max}^{C_2H_5OH}$ of 277 mμ (6 mμ higher than that of IV) and consistent with a trans-fused tetrahydrofuran ring postulated before in the corresponding methyl carbinol series (*cf.* reference 1) rapidly shifted to a shorter wave length on standing in alcohol.