to water, they were rapidly converted to *t*-butylbenzamide. The amide was prepared independently and the spectra (infrared and nmr) were identical.

Fluorination of Benzilidene-*sec*-butylamine.—The anil (7.0 g, 44 mmoles) was fluorinated in the manner described above to yield 8.5 g of crude, unstable products. The N-*sec*-butyl analog of *syn* II could be observed in this crude by infrared and nmr. Rapid elution chromatography at 10° (silica gel) produced the fluoramine (Ib, 2.2 g, 22% yield) as a colorless, unstable oil. The fluoramine must be eluted from the column within 10 min or decomposition becomes appreciable. The spectral characteristics are analogous with those of Ia and are included in the discussion section.

Anal. Calcd for $C_{11}H_{14}F_3N$: C, 60.82; H, 6.50; N, 6.45. Found: C, 59.84; H, 6.08; N, 6.29.

Rapid (10 min/10°) elution of the above oil (4.0 g) on anhydrous (150°/0.01 mm/15 hr) silica gel caused elimination of the elements of *sec*-butyl fluoride from Ib with isolation of 1.1 g of a new product, **fluorimine III.** No fluoramine (Ib) could be recovered from the column. Compound III contained bands for C=N (6.05 μ), CF (8.5–9.5 μ), and =NF (10.8 and 11.75 μ) along with the usual monosubstituted phenyl. The proton nmr spectrum contained only aromatic protons, whereas the F^{19} spectrum was two doublets of equal areas centered at ϕ +37.9 (=NF) and +77.9 (=CF) with J_{FF} = 26 cps.[11] The molecular weight determined by the mass spectral effusion method was 133 (theoretical, 141).

Anal. Calcd for $C_7H_5F_2N$: C, 59.57; H, 3.57; N, 9.93. Found: C, 59.55; H, 4.14; N, 9.38.

Hydrolysis of Ib to N-Fluoro-N-*sec*-butylbenzamide (IV).—The fluoramine (1.1 g, 5.1 mmoles) was dissolved in 5.0 ml of methanol containing 1 ml of water and 1 drop of concentrated HCl. The mixture was stirred for 1 hr at 25° and 5 ml of ice-water was added. The insoluble precipitate was extracted with ether; the ether was dried ($MgSO_4$) and stripped to yield 0.6 g (61% yield) of N-fluoro-N-*sec*-butylbenzamide. Attempts at crystallization resulted in decomposition. The infrared (C=O, 5.9–6.05 μ) and proton nmr are in accordance with the postulated structure. The single proton geminal to the NF group appears as a doublet (J_{HF} = 42 cps) of sextets (J_{HH} = 7 cps) centered at δ 4.3. The F^{19} nmr spectrum consists of a doublet (J_{HF} = 42 cps) centered at ϕ +88.9.

Fluorination of Benzilideneisobutylamine.—The anil (3.5 g, 22 mmoles) was fluorinated (33 mmoles, F_2) and chromatographed in the usual manner to afford 0.97 g (21% yield) of the fluoramine Ic. The compound had an infrared spectrum similar to those of the other isomers; the nmr spectrum is included in the discussion section. The adduct would decompose at 25° within 6 hr even when analytically pure, and could not be distilled.

Anal. Calcd for $C_{11}H_{14}F_2N$: C, 60.82; H, 6.50. Found: C, 60.00; H, 6.15.

Fluorination of Additional Anils.—The corresponding α,α-difluoro-N-fluoramines could be prepared when R = 2-pentyl, 1-phenylethyl, and isopropyl. These compounds were too unstable to purify for satisfactory elemental analyses, but the spectral (H^1 and F^{19} nmr) characteristics could be obtained and are included in the discussion section.

Fluorination of Benzilidene-*sec*-butylamine Chloride (V).—The imide chloride was prepared from the corresponding amide *via* the procedure of Ugi, Beck, and Fetzer[7] and was purified by vacuum distillation to a colorless liquid, bp 60–61° (2.5 mm). The imide chloride (4.3 g, 22 mmoles) was fluorinated in the usual manner with 33 mmoles of F_2 to yield 3.0 g (63% yield) of fluoramine Ib *after* chromatography. The spectral properties were identical with those observed of the compound prepared *via* the Schiff base.

(11) R. A. Mitsch, *J. Am. Chem. Soc.*, **87**, 328 (1965). It was noted that in $CFCl_2CF{=}NF$ the =NF appeared at ϕ^* +21.5 and =C—F at +77.2 and the infrared exhibited bands at 5.95 and 11.67 μ (CF=NF).

Acknowledgment.—We are grateful to Mr. Jack Brooks for technical assistance and to Mrs. Carolyn Haney for infrared and nmr spectra.

A New Rearrangement Product in the 6,7-Benzomorphan Series

ROBERT T. PARFITT,[1]

National Institutes of Health, Bethesda, Maryland 20014

MIKIO TAKEDA AND HIROSHI KUGITA

Osaka Research Laboratory, Tanabe Seiyaku Company, Ltd., Osaka, Japan

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6-Methoxy-2,4a,4b-trimethyl-1,2,2a,4b-tetrahydro-1H-indeno[2,1-*c*]pyridine (IIIa) has been identified as the minor product of the thionyl chloride rearrangement of 2′-methoxy-9-hydroxy-2,5,9-trimethyl-6,7-benzomorphan. The structure was assigned by nmr, ultraviolet, infrared, and mass spectral data of IIIa, the hydrogenation product IV, and the Hofmann elimination product (V). The corresponding rearrangement product (IIIb) has been isolated from Ib under identical conditions. Mechanisms for the formation of II, III, and VII from I are proposed. The pyrolysis of 2′-methoxy-9-acetoxy-2,5,9-trimethyl-6,7-benzomorphan perchlorate (VIIIa) afforded VIIa as its only rearrangement product, contrasting with VIIIb which has been reported[2] to give VIIb and IXb.

It was recently reported[2] that the pyrolysis of 9-acetoxy-2,5,9-trimethyl-6,7-benzomorphan perchlorate (VIIIb) gave mixtures of the perchlorates of 1,2,3,4-tetrahydro-1,4,4-trimethyl-9H-indeno[2,1-*b*]pyridine (IXb) and 1,2,4a,9a-tetrahydro-1,4,4a-trimethyl-9H-indeno[2,1-*b*]pyridine (VIIb). Furthermore the corresponding carbinol base of VIII (Ib), in the presence of thionyl chloride, gave the expected methylene derivative (IIb) together with a low yield of the rearrangement product (VIIb).[2,3] Lastly, it has been observed[4] that dehydration of 2′-methoxy-9-hydroxy-2,5,9-trimethyl-6,7-benzomorphan (Ia) by thionyl chloride gave three products, IIa, a monochloro derivative, and an unknown rearrangement product isomeric with IIa. This communication establishes 6-methoxy-2,4a,4b-trimethyl-1,2,4a,4b-tetrahydro-1H-indeno[2,1-*c*]pyridine (IIIa)[5] as the new rearrangement product and completes structural studies on all rearrangement products, detected, so far, in this series. (See Scheme I.)

The high-resolution proton magnetic resonance spectrum of IIIa (Table I) showed four three-proton singlets at 3.85 (OCH_3), 2.63 ($>NCH_3$), and 1.28 and 1.11 ppm (two quaternary CCH_3 resonances). In the olefinic

(1) Formerly a Visiting Associate. To whom correspondence should be addressed: Department of Pharmacy, University of Strathclyde, Glasgow, Scotland.

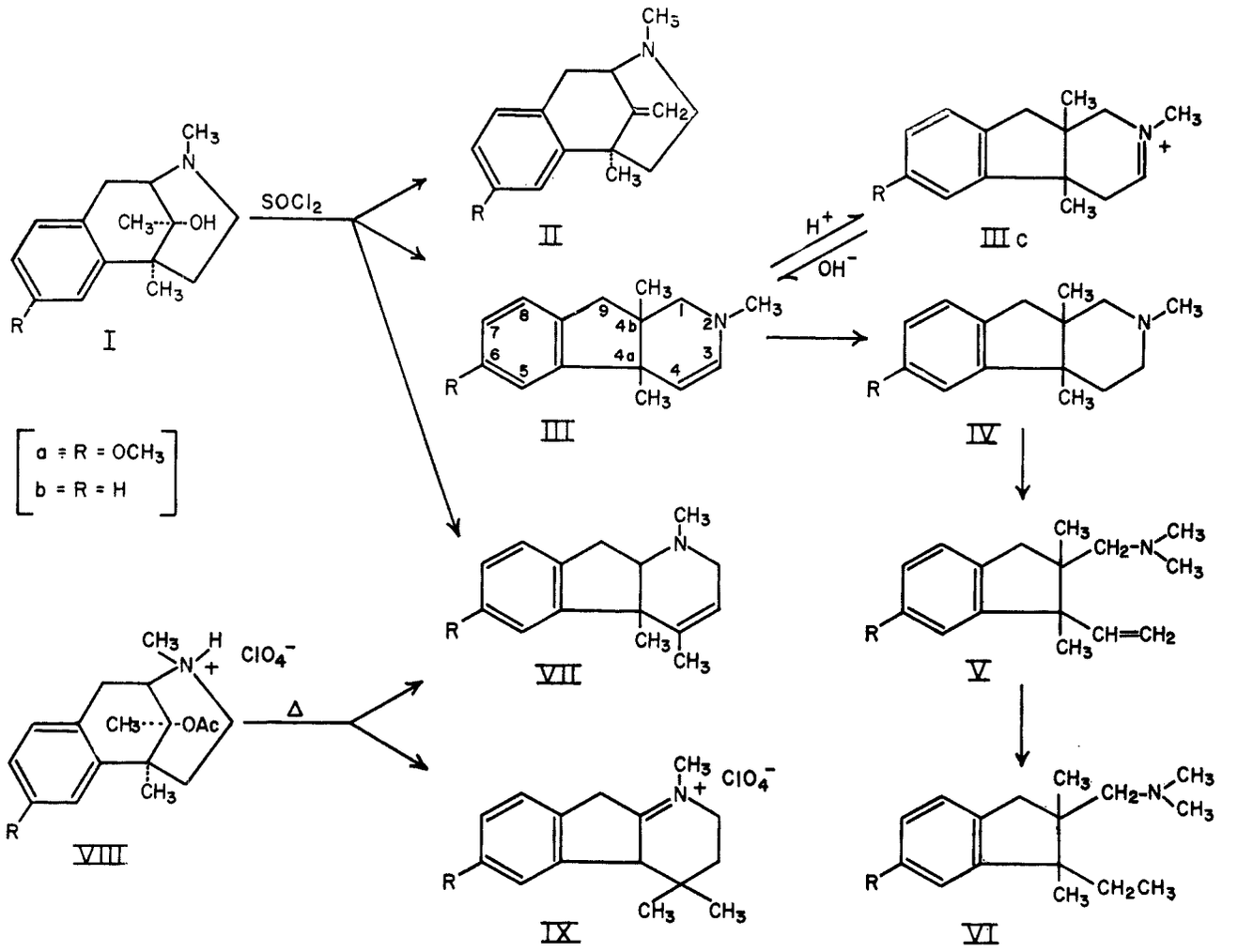
(2) R. T. Parfitt, E. M. Fry, and E. L. May, *J. Org. Chem.*, **31**, 903 (1966).

(3) H. Kugita and M. Takeda, *Chem. Pharm. Bull.* (Tokyo), **11**, 986 (1963).

(4) H. Kugita and M. Takeda, *ibid.*, **12**, 1163 (1964).

(5) 6-Methoxy-1,2a,2b-trimethyl-1,2,2a,2b-tetrahydro-2H-indeno[2,1-*c*]-pyridine is the IUPAC name for this compound.

SCHEME I



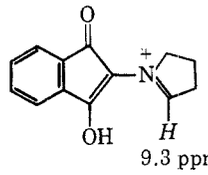
region an AX quartet (J = 8 cps) was apparent with ν_A = 4.46 ppm and ν_X = 5.87 ppm assignable to the protons on carbons 3 and 4, respectively. An AB quartet centered at 2.80 ppm ($|J|$ = 15 cps) may be assigned to the indan benzylic protons. No absorption occurred above 2 ppm except for the quaternary C–CH_3 groups. In acid solution[6] the olefinic AX pattern disappeared and was replaced by a broad single proton resonance at 9.52 ppm.[7] This is consistent with a double-bond shift from the 3,4 to the 2,3 position (III → IIIc) in tetrahydropyridine salts. Confirmation of this shift was found in the infrared spectrum. A film of the base (IIIa) adsorbed strongly at 6.1 μ (*cis* $_{H}>C=C<_{H}$), whereas in the spectrum of the hydrochloride (IIIc) in potassium bromide the band shifted to 5.9 μ (medium) ($>C=\overset{+}{N}<$).[2,8] The acid pmr spectrum displayed the expected shift of the NCH_3 downfield to 3.90 ppm; the benzylic indano protons were little affected and occurred at 2.85 ppm. Only one set of benzylic protons was observed, the 1-position protons being shifted, in the acidic solution, to a poorly resolved pattern centered at 3.5 ppm. Only substituted methoxyphenyl absorption could be seen in the ultraviolet spectrum of IIIa.

One molar equivalent of platinum-catalyzed hydrogen was absorbed rapidly by IIIa hydrochloride to give IV hydrochloride, the base of which lacked olefinic resonance in the pmr spectrum. The four three-proton singlets (Table I) occurred in the positions expected, and benzylic absorption appeared as an apparent singlet at 2.60 ppm. Methylene group resonance was present as a complex pattern between 1.5 and 2.5 ppm.

The methiodide of IV on treatment with silver oxide gave Hofmann elimination product V. The pmr spectrum of this product showed a characteristic ABX pattern ($J_{AX} + J_{BX}$ = 27.5 cps) in the olefinic region. A singlet integrating for six protons at 2.31 ppm corresponded to $N(CH_3)_2$ resonance, and three three-

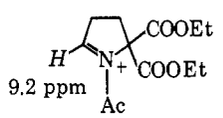
(6) Dry hydrochloric acid was passed briefly through a deuteriochloroform solution of IIIa. A similar spectrum was obtained from a solution of IIIa hydrochloride in deuteriomethanol.

(7) Similar shifts have been observed in the pmr spectra of tetrahydropyridines (A. E. Jacobson and R. T. Parfitt, in preparation), and A. Mauger (George Washington University, Washington, D. C.) has informed us of the chemical shifts of the olefinic protons in the following pyrroles (unpublished results). See, also, N. J. Leonard and J. V. Paukstells, *J. Org. Chem.*, **28**, 3021 (1963).



in trifluoroacetic acid

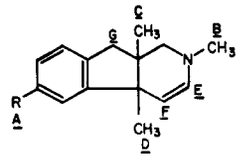
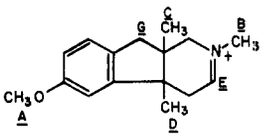
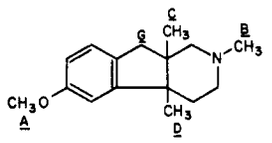
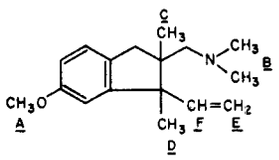
and



in sulfuric acid

(8) See N. J. Leonard and F. P. Hauck, *J. Am. Chem. Soc.*, **79**, 5279 (1957), for a leading reference regarding this shift.

TABLE I

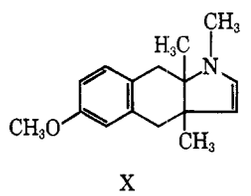
Compd		Pmr spectra[a] A	B	C	D	E	F	G
	III b	...	2.58 (s)	1.05 (s)	1.23 (s)	5.78 (d)	4.39 (d)	2.73
						J = 7.5 cps		
	III a	3.85 (s)	2.63 (s)	1.11 (s)	1.28 (s)	5.87 (d)	4.46 (d)	2.80 (q) $\|J\|$ = 15 cps
						J = 8.0 cps		
	IIIc	3.83 (s)	3.90 (s) broad	1.30 (s)		9.52	...	2.85[b]
	IV	3.77 (s)	2.12 (s)	1.03 (s)	1.11 (s)	...	...	2.60[b]
	V	3.79 (s)	2.30 (s)	1.04 (s)	1.28 (s)	ABX pattern: 8 lines	4 lines	2.78 (q) $\|J\|$ = 15 cps
						$J_{AX} + J_{BX}$ = 27.5 cps		

[a] Signals are described thus: s = singlet; d = doublet; q = quartet. [b] Apparent singlet.

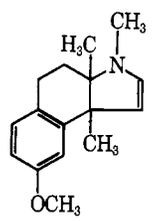
proton singlets occur as expected (Table I). An AB quartet centered at 2.78 ppm. ($|J|$ = 15 cps), assignable to the indan benzylic protons, collapsed to a two-proton singlet at 2.69 ppm, in the spectrum of the hydrochloride salt in deuteriomethanol. The ultraviolet spectrum of V displayed only substituted methoxyphenyl absorption.

Atmospheric pressure hydrogenation of V hydrochloride over platinum oxide gave VI hydrochloride, which on palladium–charcoal treatment at 305–310° afforded on oil having the ultraviolet absorption characteristics of an indene[2,9] [λ_{max} 267 mμ ($\epsilon \simeq 4000$)].

The above evidence, although strongly supporting IIIa and V as the structures of the rearrangement and Hofmann elimination products, respectively, does not completely eliminate structures X and XI. However,



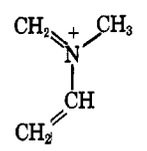
X



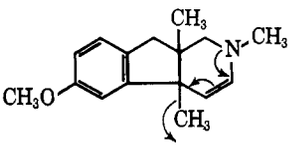
XI

further evidence for V was the failure of its methiodide to undergo Hofmann elimination. This indicated a lack of protons β to the amino group. In both X and XI double Hofmann elimination would be expected.

Confirmation of IIIa and V came from their mass spectra. Compound IIIa exhibited a strong M^+ peak at 243 and a base peak at m/e 70. The latter may be explained by cleavage of the heterocyclic ring accompanied by a proton transfer to give a fragment C_4H_8N (XII). This fragment is unlikely to result from structures X or XI. An intense P − 15 peak, expected for

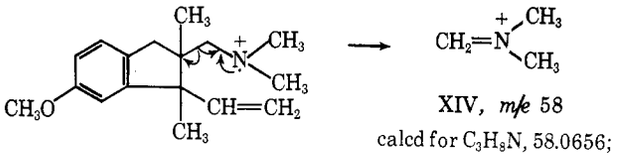


XII, m/e 70



XIII

a structure such as IIIa, probably resulted from the concerted loss of the benzylic 4a-methyl group (XIII). A moderate P − 30 peak may be accounted for by the loss of both quaternary methyl groups. The base peak of the Hofmann elimination product V at m/e 58 corresponded to the fragment C_3H_8N (XIV) from the anticipated fragmentation. A moderate parent ion



XIV, m/e 58

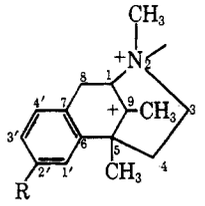
calcd for C_3H_8N, 58.0656; found, 58.06455

at m/e 259 and a weak P − 15 peak are also present. The presence of fragment XIV as the base peak of V cannot be rationalized as arising from the fragmentation of Hofmann elimination products of X and XI.

Thionyl chloride dehydration of Ib was reported[2] to give IIb as the major product, VIIb in 4% yield, and 1% of an unidentified base as the perchlorate, mp 184–185°. Analytical data have now shown that this base is isomeric with IIb, and pmr data have confirmed IIIb as the structure of this rearrangement product.

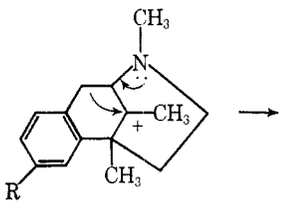
The formation of II and VII from I by thionyl chloride treatment may be rationalized as being *via* a common carbonium ion intermediate (XV). Collapse of the carbonium ion with the removal of a proton from one of the three available positions (positions 4-, 8-, and 9-methyl) would lead to three possible products.

(9) T. L. Yarboro, C. Karr, and P. A. Estep, *J. Chem. Eng. Data*, **6**, 421 (1961).

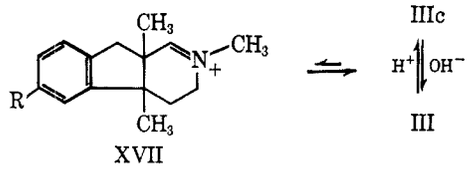


XV

However, reference to a Dreiding model of I shows the most acidic 8-position protons to be sterically hindered to base participation, whereas those of the 9-methyl and 4 positions are readily available. Proton elimination from the 9-methyl group would lead to II, whereas VII could be formed by loss of a 4-position proton, after equilibration of the carbonium ion to position 5. Compound III, in low yield, could be derived from carbonium ion formation (XVI) prior to salt formation, in which case participation of the nonbonding nitrogen electrons could lead to XVII[10] tautomeric with IIIc.[11]



XVI



XVII

Finally, the pyrolysis of 2′-methoxy-9-acetoxy-2,5,9-trimethyl-6,7-benzomorphan perchlorate (VIIIa) has been investigated. At 184° for 2 min, it affords 58% of the rearrangement product VIIa perchlorate, which was identified by comparison of the pmr spectrum of the base[12] with that of VIIb.[2] Monitoring of the reaction with glpc during 30 min showed VIIa to be the only significant product. In contrast with the pyrolysis of VIIIb, no product corresponding to IXa could be detected. This may be accounted for by the susceptibility of IXa to oxidation, which a 2′-methoxy group might be expected to enhance. Continuation of the pyrolysis beyond the optimum time of 2 min resulted in an increasing amount of intractable tar. After 30 min no product could be isolated.

Experimental Section

Melting points were taken in a capillary and are uncorrected. Pmr spectra were determined in $CDCl_3$ (unless stated otherwise), with shifts reported in ppm downfield from tetramethylsilane as an internal reference (Varian Model A-60). Mass spectra were determined on an Associated Electronic Industries, MS-9 double-focussing mass spectrometer. Accurate mass measurements were made relative to perfluorokerosene internal standard, (C = 12.000).

6-Methoxy-2,4a,4b-trimethyl-1,2,4a,4b-tetrahydro-1H-indeno[2,1-*c*]pyridine (IIIa) Hydrochloride.—This compound was isolated as its monohydrate by the method of Kugita and Takeda.[4] It crystallized as colorless needles: mp 163–165° dec, from acetone–ethanol–ether, λ_{max}^{Nujol} 3.2 μ (water), λ_{max}^{EtOH} 284 mμ (ϵ 4380). *Anal.* Calcd for $C_{16}H_{22}ClNO \cdot H_2O$: C, 64.52; H, 8.13; N, 4.70. Found: C, 64.51; H, 8.25; N, 4.92.

6-Methoxy-2,4a,4b-trimethyl-1,2,3,4,4a,4b-hexahydro-1H-indeno[2,1-*c*]pyridine (IV) Hydrochloride.—Compound IIIa hydrochloride (1.24 g), ethanol (50 ml), and platinum oxide (180 mg) absorbed 1 molar equiv of hydrogen in 5 min. The resultant **IV hydrochloride** (1.03 g, 82%) was recrystallized from acetone–methanol–ether as colorless needles: mp 232–234° dec, λ_{max}^{EtOH} 283 and 289 mμ (ϵ 3390 and 2980). *Anal.* Calcd for $C_{16}H_{24}ClNO$: C, 68.20; H, 8.58; N, 4.97. Found: C, 67.90; H, 8.33; N, 5.05.

The **methiodide**, prepared in 95% yield, from an acetone solution of the base and methyl iodide, gave needles, mp 273–275° dec, from methanol. *Anal.* Calcd for $C_{17}H_{26}INO$: C, 52.72; H, 6.77; N, 3.62. Found: C, 53.01; H, 6.76; N, 3.30.

2-Dimethylaminomethyl-3-vinyl-5-methoxy-2,3-dimethylindan (V).—The methiodide of IV (300 mg) was treated with silver oxide (from 270 mg of silver nitrate) in water for 1 hr and filtered. The solution was heated under reflux for 3 hr (no oil separated). Evaporation of the filtrate to dryness, and distillation *in vacuo* of the residue [100–104° (0.8 mm)] gave product V (190 mg, 94%): λ_{max}^{film} 9.95 and 10.95 μ, λ_{max}^{MeOH} 281 and 288 mμ (ϵ 3100 and 2780).

The **hydrochloride** crystallized from acetone–ethanol–ether as colorless needles: mp 203–204° dec, λ_{max}^{Nujol} 9.85 and 10.95 μ. *Anal.* Calcd for $C_{17}H_{26}ClNO$: C, 69.01; H, 8.86; N, 4.74. Found: C, 68.63; H, 8.60; N, 4.61.

2-Dimethylamino-3-ethyl-5-methoxy-2,3-dimethylindan (VI).—Hydrogenation of V hydrochloride (150 mg) in ethanol (35 ml) over platinum oxide (50 mg) for 40 min, gave **VI hydrochloride** (150 mg, 98%), mp 229–231° dec. It was recrystallized from acetone–ethanol–ether as colorless needles, mp 232–233° dec. *Anal.* Calcd for $C_{17}H_{28}ClNO$: C, 68.55; H, 9.48; N, 4.70. Found: C, 68.48; H, 9.29; N, 4.60.

The **methiodide**, prepared in acetone solution, was recrystallized from methanol, mp 271–273° dec. *Anal.* Calcd for $C_{18}H_{30}INO$: C, 53.60; H, 7.50; N, 3.47. Found: C, 53.55; H, 7.15; N, 3.66.

Dehydrogenation of VI.—A mixture of VI (130 mg) and 130 mg of 10% Pd–C was heated at 305–310° (metal bath) for 25 min, cooled, and extracted with ether. The ether solution was washed with 5% aqueous HCl and water, dried, and evaporated. Distillation of the residue gave a colorless oil (60 mg): bp 100–130° (1 mm), λ_{max}^{MeOH} 267 mμ ($\epsilon \simeq 4000$).

2,4a,4b-Trimethyl-1,2,4a,4b-tetrahydro-1H-indeno[2,1-*c*]pyridine (IIIb) Perchlorate.—This compound was isolated according to the method of Parfitt, Fry, and May.[2] It was recrystallized from acetone–ether as colorless prisms, mp 184–185°. *Anal.* Calcd for $C_{15}H_{20}ClNO_4$: C, 57.41; H, 6.43; N, 4.47. Found: C, 57.35; H, 6.48; N, 4.40.

Pyrolysis of 2′-Methoxy-2,5,9-trimethyl-7-benzomorphan Perchlorate (VIIIa).—Compound VIIIa (0.5 g) was heated at 184° (aniline vapor bath) for 2 min (rapid evolution of acetic acid). The resultant, cooled, dark oil was dissolved in ethanol and ethyl acetate was added. **6-Methoxy-1,2,4a,9a-tetrahydro-1,4,4a-trimethyl-9H-indeno[2,1-*b*]pyridine VIIa perchlorate**, mp 215–218°, separated during 2 days. It was recrystallized from acetone–ethyl acetate as colorless prisms: mp 221–222° dec; pmr (δ) of VIIa (free base), 4a-CH_3 (1.56, singlet), 4-CH_3 (1.63, doublet, J = 1.5 cps), NCH_3 (2.50, singlet), OCH_3 (3.82, singlet), olefinic 3-position proton (5.36, multiplet). *Anal.* Calcd for $C_{16}H_{22}ClNO_5$: C, 55.90; H, 6.45; N, 4.08. Found: C, 56.11; H, 6.19; N, 4.17.

Acknowledgments.—We are indebted to Dr. H. M. Fales of the National Heart Institute for determination of the mass spectra and to Drs. E. L. May and A. E. Jacobson for valuable discussions.

(10) Resonance from XVII was not observed in the pmr spectrum of III in acid solution.

(11) Prototrophic isomerization of this type is highly dependent upon steric factors. In this case hindrance of position 1 in IIIc would prevent isomerization back to XVII. See N. J. Leonard, K. Conrow, and R. R. Sauers, *J. Am. Chem. Soc.*, **80**, 5185 (1958).

(12) See the Experimental Section.