Registry No.—Sodium *p*-toluenethiolate, 10486-08-5.

Acknowledgments.—This work was supported by Grant No. GP 12326 from the National Science Foundation, for which we are grateful. A portion of this work was presented at the 161st National Meeting of the American Chemical Society on March 31, 1971, and was taken from the Ph.D. Thesis of G. J. W. T., Purdue University, Aug 1970.

Stereochemistry of Amido Derivatives of 3a,4,5,6-Tetrahydroindan and Related Compounds

BARTLETT D. WHELTON[1] AND ALAIN C. HUITRIC*

College of Pharmacy, University of Washington, Seattle, Washington 98195

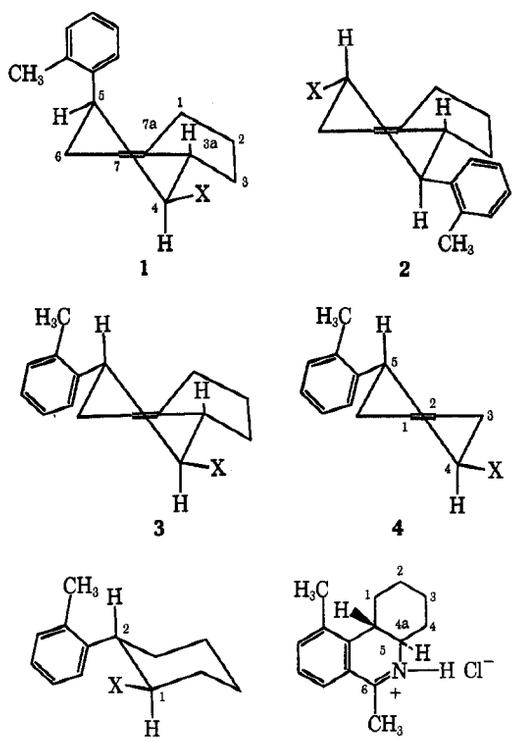
Received July 19, 1971

Three isomeric 5-*o*-tolyl-4-nitro- and 4-*o*-tolyl-5-nitro-3a,4,5,6-tetrahydroindans and 4-nitro-5-*o*-tolylcyclohexene were converted to the corresponding amines with retention of stereochemistry by reduction with iron in acetic acid. Rotational isomerism of the formamide, acetamide, and *N*-methylacetamide derivatives of the amines was studied by nmr. Two rotational isomers were seen in deuteriochloroform for all amides except the acetamides. The geometry of the major amide conformers is discussed. Of special interest from a conformational standpoint is the observation of a predominance of the half-chair conformation with the *o*-tolyl group occupying an axial orientation in the series of *cis*-4-amino-*cis*-*o*-tolyl-3a,4,5,6-tetrahydroindan and corresponding amides.

The nmr characterization of isomeric 5-*o*-tolyl-4-nitro- and 4-*o*-tolyl-5-nitro-3a,4,5,6-tetrahydroindans was reported earlier.[2] We now report the preparation of amines **1a–4a** in quantitative yields by iron in acetic acid reduction[3,4] of the corresponding nitro compounds of established stereochemistry[2,3] and an nmr investigation of rotational isomerism in derived amides of **1a–5a**. Retention of configuration at the nitro-bearing carbon during the iron in acetic acid reduction[3] is substantiated by the splitting pattern and/or width of the signal of the hydrogen on the nitrogen-bearing carbon of the resulting amine and amide derivatives. Migration of the double bond during the synthesis of the amino- and amidocyclohexenes **4** is ruled out on the basis of the integration of the olefinic hydrogens and the multiplicities and widths of the signals of the hydrogens at the functional group bearing carbons. The proof is not as unequivocal for the tetrahydroindan derivatives **1–3**, but two of the three possible products of simple migration are ruled out on similar grounds and the third, resulting in a 6,7-disubstituted 2,4,5,6,7,7a-hexahydroindene, seems an unlikely candidate from a thermodynamic stability standpoint. If any migration had occurred, mixtures would be expected.

Because of the fixed orientation of the bridgehead H-3a, only one half-chair conformation is possible for the tetrahydroindan compounds **1–3**, but boat and other flexible conformations are not ruled out. On the basis of the coupling patterns and/or widths of the signals of the hydrogens on the functional group bearing carbons (J_{aa} values are normally around 10–11 Hz, and J_{ae} and J_{ee} are usually in the neighborhood of 3.5 Hz) the nmr spectra in $CDCl_3$ indicate a time-average predominance of the conformations shown in Chart I. This is expected for all compounds of series **2–5**, where the substituents are trans and where the diequatorial conformation is preferred, but it is not as predictable for compounds of series **1**. In series **1** the spectra of **1a**, **1b**, **1d**, and **1e** are very informative. For **1a** in trichloroethylene the signal of H-4 gives a doublet of doublets, $J_{43a} = 8.5$ and $J_{45} = 4.5$ Hz, indicative of a predominance of the conformer with H-4 in axial orientation. The signal of H-5 gives a seven-peak multiplet with width of 12.4 Hz. The splitting pattern indicates $J_{56(ax)} = 6.2$, $J_{56(eq)} = 1.7$, and $J_{54} = 4.5$ Hz.

CHART I



a, X = NH_2
b, X = NHCHO
c, X = $^{+}NH_2CH_3Cl^-$
d, X = NCH_3COCH_3
e, X = $NHCOCH_3$

(1) Public Health Service Predoctoral Fellow 5-FO1-GM-34,830, 1967–1969.
(2) B. D. Whelton and A. C. Huitric, *J. Org. Chem.*, **36**, 1480 (1971).
(3) W. F. Trager, F. F. Vincenzi, and A. C. Huitric, *ibid.*, **27**, 3006 (1962).
(4) N. Kornblum, W. D. Burowitz, H. O. Larsen, and D. E. Hardies, *J. Amer. Chem. Soc.*, **82**, 3099 (1960).

The seven-peak multiplet results from overlapping of the two inner components of what would otherwise be an eight-peak multiplet. The signal indicates a predominance of the conformer where H-5 has the equatorial orientation. For **1b** in $CDCl_3$, after deuterium exchange of the NH hydrogen, the signal of H-4 appears as a doublet of doublets, $J_{43a} = 10.0$ and $J_{45} = 4.7$ Hz, and the width of the signal of H-5 is 12 Hz, again consistent with a predominance of the conformer with H-4 axial and H-5 equatorial. For **1d** in $CDCl_3$ the signal of H-4 also gives a doublet of doublets, $J_{43a} = 11.0$ and $J_{45} = 4.6$ Hz. For **1e** the width of the signal of H-5 is again about 12 Hz and the signal of H-4 appears as a six-peak multiplet indicative of $J_{43a} \cong J_{4NH} \cong 9.7$ and $J_{45} \cong 4.7$ Hz. The NH signal appears as a broad doublet at δ 5.27, $J_{NH,4} \cong 9.7$ Hz. The data again support a predominance of the half-chair conformation with the aromatic ring occupying an axial orientation. The signals of H-5 in the spectra of **1b** and **1e** appear essentially as multiplets having three fairly broad components which suggest coupling constants of slightly over 6 Hz between H-5 and pseudoaxial H-6, about 1 Hz, or less, between H-5 and equatorial H-6, and about 4.7 Hz between H-5 and H-4 as seen from the signals of H-4. Molecular models show that the dihedral angle between H-5 and equatorial H-6, in the proposed conformation, is close to 90° and explains the very small coupling constant between these hydrogens.

The nmr spectra of the formamides **1b–5b** and the four *N*-methyl acetamides investigated (**1d**, **3d**, **4d**, and **5d**) all show the presence of two rotational conformers resulting from slow rotation, on the nmr time scale, about the C–N bond of the amido group. A fairly rough approximation by integration indicates a ratio of conformers of about 3:1 in deuteriochloroform. The presence of two conformers could be detected from differences in chemical shifts of the signals of some of the following groups between the two conformers: CHO, HN, NCH_3, $ArCH_3$, PhCH, $COCH_3$, and the hydrogen on the amido-bearing carbon. It is interesting to note that rotational conformers were not detected in any of the secondary acetamides investigated, compounds **1e**, **4e**, and **5e**. This does not imply a more rapid rotation about the C–N bond but suggests a position of the equilibrium in favor of essentially only one conformer. Published data on isomerism of secondary amides[5] indicate a usual predominance of the isomer having a trans orientation of the N substituent and the R or H on the carbonyl carbon. Our results with the five formamides are in agreement with this. In all formamides the signal of the formyl hydrogen of the major isomer gives an arrow doublet, $J = 2$ Hz, while that of the minor isomer gives a coupling constant of 12 Hz between the formyl and NH hydrogens. This is consistent with a trans orientation of these two hydrogens in the minor isomers and cis in the major. Deuterium exchange of the NH hydrogen causes each of these two signals to collapse to a singlet. In deuteriochloroform the signal of the formyl hydrogen of the major isomer was always the furthest downfield and the difference was most pronounced for compounds **2b–5b**. This is as expected because in the minor isomer, having the formyl hydrogen cis to the N substituent, the formyl hydrogen comes closer to the face, and thus the shielding region, of the aromatic ring. A comparison of the chemical shifts of the hydrogen on the amido-bearing carbon (XCH) and of the tolyl methyl group ($ArCH_3$) between acetamides **1e**, **4e**, and **5e** with the respective signals of the major conformers of formamides **1b**, **4b**, and **5b** suggests that the acetamides also have the trans orientation between the acetyl methyl group and the N substituent. For the XCH signal the differences in chemical shifts between the acetamides and the major conformers of the corresponding formamides are 0.09, 0.02, and 0.0 ppm for series **1**, **4**, and **5**, respectively, and for the $ArCH_3$ signals the differences are 0.02, 0.03, and 0.02, respectively. The formamide **2b** was investigated at higher temperature in tetrachloroethylene. Merging of the corresponding signals of the two conformers occurred between 120 and 130°. The data are given in the Experimental Section. At 130° the signal of the formyl hydrogen appears as a doublet with separation of 4.4 Hz. This represents the average coupling constant between the CHO and NH hydrogens in the more rapidly rotating system. On the basis of coupling constants of 2.0 and 12.0 Hz in the major and minor frozen conformers, and of 4.4 Hz in the mobile system at elevated temperature, the calculated time-average proportions of conformers at 130° is 76% of the major and 24% of the minor. Since the calculation involves differences in widths between fairly narrow signals, small errors in measurements of signal widths can introduce fairly large errors in calculated values. At the normal operating temperature of 37° the ratio, from integration of signals, was about 4:1 in tetrachloroethylene.

The Bischler–Napieralski cyclization[6] of **5e**, by refluxing with phosphorus oxychloride in chlorobenzene, yielded the 6,10-dimethyl-4a,10b-*trans*-1,2,3,4,4a,10b-hexahydrophenanthridine (the free amine of **6**). The nmr spectrum of the product obtained from treatment of **4e** under similar conditions suggests that random migration of the double bond has occurred. In compound **6**, and the corresponding free imine, the nmr signal of the methyl group at C-6 appears as a doublet with separation of 1.5 Hz. The splitting is attributed to homoallylic coupling[7] with H-4a.

Experimental Section

The nmr spectra were recorded on a Varian A-60 spectrometer at a temperature of ~37°, unless stated otherwise, utilizing ~20% (w/v) solutions with tetramethylsilane (TMS) as the internal reference. High-temperature studies were accomplished using the Varian HR-60 spectrometer. Infrared spectra were determined using a Beckman IR-5-A infrared spectrometer. Melting points were determined on the Kofler micro hot stage (K) equipped with a factory-calibrated thermometer or on the Thomas-Hoover capillary melting point apparatus (TH). Elemental analyses were conducted by the Huffman Laboratories, Wheatridge, Colo.

Primary amines 1a, 2a, 3a, and 4a were prepared by iron and acetic acid reduction of the known parent nitro compounds[2,3] by a method described by Kornblum and coworkers[4] for the synthesis of (+)-α-phenylethylamine. Quantitative recovery of each free amine as a light orange oil from its basified reaction mixture

(5) W. E. Stewart and T. H. Siddall, III, *Chem. Rev.*, **70**, 517 (1970).

(6) W. M. Whaley and T. R. Govindachari, *Org. React.*, **6**, 74 (1951).

(7) L. M. Jackman and S. Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Elmsford, N. Y., 1969, p 326.

was achieved by using a continuous extractor with diethyl ether as solvent. A sample of each oil taken for vpc analysis on a 10 ft × 0.125 in. column of 10% QF-1 (Fluoro Silicone) on 60/80 mesh acid washed Chromosorb W at 215° indicated that reduction was complete and that none of the parent nitro derivative was present. These four amines were not further purified but were used directly to synthesize their corresponding formamide and acetamide derivatives. Nmr of free bases (C_2Cl_4) follows: **1a**, δ 5.53 (m, 1, =CH), 3.45 (seven-peak m, 1, J = 6.2, 4.5, 1.7 Hz, PhCH), 2.68 (dd, 1, J = 8.5, 4.5 Hz, XCH), 2.44 (s, 3, $ArCH_3$); **2a**, δ 5.42 (m, 1, =CH), ~3.1 (broad m, 1, XCH), ~2.55 (partially overlapped, poorly resolved triplet, separation of ~10 Hz, PhCH), 2.33 (s, 3, $ArCH_3$); **3a**, δ 5.40 (m, 1, =CH), ~2.85 (broad m, 2, XCH and PhCH), 2.33 (s, 3, $ArCH_3$); **4a**, δ 5.53 (m, 2, =CH), ~2.98 (broad m, 2, XCH and PhCH), 2.33 (s, 3, $ArCH_3$).

Formamides 1b, 2b, 3b, and 4b were synthesized by refluxing the appropriate primary amine in redistilled 99% formic acid (10 molar equiv excess) with dry toluene in a manner essentially described by McKusick and Webster[8] for *N*-*o*-tolylformamide. When necessary the individual formamide was further purified by descending dry column chromatography[9] utilizing diethyl ether to eliminate the dark material and then further eluting with diethyl ether–acetone mixtures to recover the formamide.

cis-**4-Formamido-*cis*-5-*o*-tolyl-3a,4,5,6-tetrahydroindan (1b)**[10] was recrystallized from benzene–*n*-hexane (73%): mp 161.4–164.3° (K); ir (KBr) 1565, 1650 (C=O), 2885 (formyl CH), 2945, and 3220 cm^{-1} (NH); nmr ($CDCl_3$) δ 7.98 (d, <1, J = 2 Hz, CHO, major), 7.95 (d, <1, J = 12 Hz, CHO, minor), 5.62 (m, 1, =CH), 4.17 (m, <1, XCH, gives dd, J = 10 and 4.7 Hz, after deuterium exchange of the NH hydrogen), 3.65 (m, $W_{1/2}$ = 12 Hz, ArCH), 2.32 (s, 3, $ArCH_3$).

Anal. Calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49. Found: C, 79.60; H, 8.13; N, 5.49.

cis-**4-*o*-Tolyl-*trans*-5-formamido-3a,4,5,6-tetrahydroindan (2b)**[10] was recrystallized from benzene–*n*-hexane: mp 110.1–112.8° (K); ir (KBr) 1540, 1660 (C=O), 2875 (formyl CH), and 3270 cm^{-1} (NH); nmr ($CDCl_3$) δ 7.70 (d, <1, J = 2 Hz, CHO, major), 7.48 (d, <1, = 12 Hz, CHO, minor), ~5.84 (m, <1, NH, major), ~6.30 (m, <1, NH, minor), 5.44 (m, 1, =CH), 4.43 (m, <1, W >30 Hz, XCH, major), 3.65 (m, <1, XCH, minor), 2.85 (t, <1, $J \cong$ 10.5 Hz, ArCH, major), 2.78 (t, <1, $J \cong$ 10.5 Hz, ArCH, minor), 2.32 (s, <3, $ArCH_3$ major), 2.23 (s, <3, $ArCH_3$, minor); nmr (C_2Cl_4) at 37° δ 7.22 (d,[11] CHO, major), 7.18 (d,[11] CHO, minor), 5.34 (m, 1, =CH), 4.30 (m, <1, W >30 Hz, XCH, major), 3.42 (m, <1, XCH, minor), 2.77 (t,[12] $J \cong$ 10 Hz, ArCH), 2.21 (s, <3, $ArCH_3$, major), 2.11 (s, <3, $ArCH_3$, minor); nmr (C_2Cl_4) at 130° δ 7.42 (d, 1, J = 4.4 Hz, CHO), 5.87 (m, 1, NH), 5.31 (m, 1, =CH), 4.05 (m, 1, W >30 Hz, XCH), 2.76 (t, 1, J = 10 Hz, ArCH), 2.19 (s, 3, $ArCH_3$).

Anal. Calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49. Found: C, 80.12; H, 8.27; N, 5.62.

cis-**4-Formamido-*trans*-5-*o*-tolyl-3a,4,5,6-tetrahydroindan (3b)**[10] was recrystallized from benzene: mp 155.9–159.0° (K); ir (KBr) 1550, 1655 (C=O), 2860 (formyl CH), and 3200 cm^{-1} (NH); nmr ($CDCl_3$) δ 7.77 (d, <1, J = 2 Hz, CHO, major), 7.57 (d, <1, J = 12 Hz, CHO minor), 5.80 (broad d, <1, separation ~10 Hz, NH, major), 5.49 (m, 1, =CH), 4.25 (q, $J \cong$ 10 Hz, XCH, major, gives essentially a triplet, J = 10 Hz, after deuterium exchange of NH hydrogen), 3.21 (m, $W \cong$ 27 Hz, PhCH, major), 2.31 (s, <3, $ArCH_3$, major), 2.24 (s, <3, $ArCH_3$, minor).

Anal. Calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49. Found: C, 79.48; H, 8.23; N, 5.48.

trans-**4-Formamido-5-*o*-tolylcyclohexene (4b)** was recrystallized from benzene–*n*-hexane: mp 96.8–98.5° (K); ir (KBr) 1550, 1655 (C=O), 2890 (formyl CH), and 3220 cm^{-1} (NH); nmr ($CDCl_3$) δ 7.80 (d, <1, J = 2 Hz, CHO, major), 7.61 (d, <1, J = 12 Hz, CHO, minor), 6.11 (m, <1, NH, major), 5.77 (m, 2, =CH), 4.43 (m, <1, $W \cong$ 32 Hz, XCH major), 3.21 (m, $W \cong$ 25 Hz, ArCH, major), 2.35 (s, <3, $ArCH_3$, major), 2.27 (s, <3, $ArCH_3$, minor).

Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 78.40; H, 7.98; N, 6.51.

The *N*-methylammonium salts **1c, 3c, 4c,** and **5c** were prepared by lithium aluminum hydride reduction of the respective formamide precursors by a method essentially described by Cope and Ciganek[13] for the synthesis of *N*,*N*-dimethylcyclohexylmethylamine. Each secondary amine was then dissolved in diethyl ether and treated with a solution of concentrated hydrochloric acid in methanol.

cis-**4-*N*-Methylamino-*cis*-5-*o*-tolyl-3a,4,5,6-tetrahydroindan hydrochloride (1c)**[10] was recrystallized from diethyl ether and absolute ethanol (63%): mp 224.0–227.0° (TH, sealed capillary); ir (KBr) 2450, 2700 cm^{-1} (NH); nmr (95% HCOOH–5% D_2O) δ 5.72 (m, 1, =CH), 3.82 (m, 1, ArCH), 3.53 (m, 1, XCH), (the signal at 3.82 is narrower than the one at 3.53 but partial overlap of the two signals precludes width measurement), 2.92 (five-peak m with separation of 2.8 Hz,[14] 3, NCH_3), 2.45 (s, 3, $ArCH_3$); nmr of free base (C_2Cl_4) δ 5.56 (m, 1, =CH), 3.51 (m, 1, $W \cong$ 12.5 Hz, ArCH), 2.42 (s, 3, NCH_3 or $ArCH_3$), 2.40 (s, 3, NCH_3 or $ArCH_3$). Mass spectral analysis of the molecular ion gave m/e 241.1852 (calcd for $C_{17}H_{23}N$: 241.1828). The mass spectral analysis was carried out on the hydrochloride salt. The loss of HCl is a normal fragmentation for hydrochloride salts of amines.

Anal. Calcd for $C_{17}H_{24}ClN$: C, 73.49; H, 8.71; N, 5.04. Found: C, 72.93; H, 8.70; N, 5.07.

cis-**4-*N*-Methylamino-*trans*-5-*o*-tolyl-3a,4,5,6-tetrahydroindan hydrochloride (3c)**[10] was recrystallized from diethyl ether and absolute ethanol (81%): mp 258.5–259.0° (TH, sealed capillary); ir (KBr) 2450 and 2650 cm^{-1} (NH); nmr (95% HCOOH–5% D_2O) δ 5.86 (m, 1, =CH), 3.63 (broad m, 2, XCH and ArCH), 2.80 (five-peak m with separation of 2.8 Hz,[14] 3, NCH_3), 2.42 (s, 3, $ArCH_3$); nmr of free base (C_2Cl_4) δ 5.41 (m, 1, =CH), 3.11 (m, 1, $W \cong$ 26 Hz, ArCH), 2.35 (s, 3, $ArCH_3$), 2.17 (s, 3, NCH_3).

Anal.. Calcd for $C_{17}H_{24}ClN$: C, 73.49; H, 8.71; N, 5.04. Found: C, 73.43; H, 8.69; N, 5.03.

trans-**4-*N*-Methylamino-5-*o*-tolylcyclohexene hydrochloride (4c)** was recrystallized from diethyl ether and absolute methanol: mp 227.0–229.0° (TH, sealed capillary); ir (KBr) 2730 cm^{-1} (NH); nmr (95% HCOOH–5% D_2O) δ 5.87 (m, 2, =CH), 3.85 (m, 1, XCH), 3.51 (m, 1, $W \cong$ 27 Hz, ArCH, partially overlapped with signal at 3.85, not as broad), 2.86 (five-peak m,[14] 3, NCH_3), 2.42 (s, 3, $ArCH_3$).

Anal. Calcd for $C_{14}H_{20}ClN$: C, 70.72; H, 8.48; N, 5.89. Found: C, 70.87; H, 8.44; N, 5.90.

trans-**2-*o*-Tolyl-*N*-methylaminocyclohexane hydrochloride (5c)** was recrystallized from diethyl ether and absolute methanol: mp 197.7–200.2° (TH, sealed capillary); ir (KBr) 2425 and 2730 cm^{-1} (NH); nmr (95% HCOOH–5% D_2O) δ ~3.60 (m, W < 30 Hz, 1, XCH), ~3.17 (m, 1, ArCH), 2.78 (five-peak multiplet,[14] 3, NCH_3), 2.40 (s, 3, $ArCH_3$); nmr of free base (C_2Cl_4) δ ~2.61 (m, 2, XCH and ArCH), 2.32 (s, 3, $ArCH_3$), 2.15 (s, 3, NCH_3).

Anal. Calcd for $C_{14}H_{22}ClN$: C, 70.12; H, 9.25; N, 5.84. Found: C, 70.02; H, 9.17; N, 5.85.

Refluxing the respective free bases of the *N*-methylammonium salts **1c, 3c,** and **4c** with acetic anhydride in benzene afforded the *N*-methylacetamides **1d, 3d,** and **4d.** Both **1d** and **3d** were purified by dry column chromatographic techniques[9] utilizing diethyl ether as elution solvent, but neither could be crystallized. The nmr and ir of their respective oils were consistent with the expected products, however.

cis-**4-*N*-Methylacetamido-*cis*-5-*o*-tolyl-3a,4,5,6-tetrahydroindan (1d)**[10] had ir (neat) 1640 cm^{-1} (C=O); nmr ($CDCl_3$) δ 5.60

(8) B. C. McKusick and O. W. Webster, *Org. Syn.*, **41**, 102 (1961), footnote 2.

(9) B. Loev and M. M. Goodman, *Chem. Ind. (London)*, 2026 (1967).

(10) In the nomenclature adopted for the tetrahydroindans, the configuration of substituents (cis or trans) is related to the pseudoaxial bridgehead hydrogen on C-3a.

(11) The signals for both conformers are overlapped with the NH signal. The chemical shifts were obtained from the singlets resulting after deuterium exchange of the NH hydrogen.

(12) The components of the triplet are somewhat broad, suggesting a slight difference in chemical shift of the signal for the two conformers. The triplet sharpens at 130°.

(13) A. C. Cope and E. Ciganek, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 339.

(14) In pure formic acid the signal is a triplet, J = 5.6 Hz. In the presence of D_2O the doublet of the monodeuterated methylamminium ion is superimposed over the triplet, leading to the five-peak multiplet. Any dideuterated species will enhance the center component of the multiplet. Addition of more D_2O causes disappearance of the outer components of the multiplet to eventually give a three-peak multiplet with separation of 2.8 Hz resulting from a mixture of mono- and dideuterated species.

(m, 1, =CH), 4.60 (dd, <1, J = 11.0 and 4.6 Hz, XCH, major), 3.75 (m, >1, ArCH and XCH, minor), 2.23 (s, 3, $ArCH_3$ or NCH_3), 2.20 (s, 3, NCH_3 or $ArCH_3$), 2.17 (s, <3, $COCH_3$, minor), 2.05 (s, <3, $COCH_3$, major).

cis-4-*N*-**Methylacetamido**-*trans*-**5**-*o*-**tolyl-3a,4,5,6-tetrahydroindan** (**3d**)[10] had ir (neat) 1640 cm^{-1} (C=O); nmr ($CDCl_3$) δ 5.43 (m, 1, =CH), 5.08 (dd, <1, J = 11.0 and 10.0 Hz, XCH, major), 3.95 (dd, <1, XCH, minor), ~3.2 (m, ~1, $W \cong 14$ Hz, ArCH), 2.59 (s, <3, NCH_3, minor), 2.54 (s, <3, NCH_3, major), 2.35 (s, ~3,[15] $ArCH_3$), 2.13 (s, ≪3, either $ArCH_3$ or $COCH_3$ from minor conformer), 1.82 (s, ~3,[15] $COCH_3$).

trans-4-*N*-**Methylacetamido-5-***o*-**tolylcyclohexene** (**4d**) was recrystallized from *n*-hexane in 89% yield: mp 89.8–90.8° (K); ir (KBr) 1635 cm^{-1} (C=O); nmr ($CDCl_3$) δ 5.75 (m, 2, =CH), 5.32 (m, <1, $W \cong 30$ Hz, XCH, major), ~4.3 (m, <1, XCH, minor), 3.21 (m, ~1, $W \cong 27$ Hz, ArCH), 2.52 (s, 3, NCH_3), 2.36 (s, ~3,[15] $ArCH_3$), 2.18 (s, ≪3,[15] either $ArCH_3$ or $COCH_3$ from minor conformer), 1.83 (s, ~3,[15] $COCH_3$).

Anal. Calcd for $C_{16}H_{21}NO$: C, 78.97; H, 8.70; N, 5.76. Found: C, 79.12; H, 8.39; N, 5.82.

Treatment of primary amines **1a** and **4a** with acetic anhydride in dry pyridine afforded the acetamido derivatives **1e** and **4e**.

cis-**4-Acetamido**-*cis*-**5**-*o*-**tolyl-3a,4,5,6-tetrahydroindan** (**1e**)[10] was recrystallized from benzene–*n*-hexane (95%): mp 199.8–202.3° (K); ir (KBr) 1545, 1645 (C=O), 3280 cm^{-1} (NH); nmr ($CDCl_3$) δ 5.61 (m, 1, =CH), 5.27 (d, 1, $J \cong 9.7$ Hz, NH), 4.08 (dt, 1, $J \sim 9.6$, 5.0 Hz, XCH), 3.65 (m, 1, W = 11.8 Hz, ArCH), 2.30 (s, 3, $ArCH_3$), 1.83 (s, 3, $COCH_3$). Mass spectral analysis of the molecular ion gave m/e 269.1770 (calcd for $C_{18}H_{23}NO$: 269.1778).

Anal. Calcd for $C_{18}H_{23}NO$: C, 80.25; H, 8.61; N, 5.20. Found: C, 80.74; H, 8.58; N, 5.28.

trans-**4-Acetamido-5-***o*-**tolylcyclohexene** (**4e**) was recrystallized from benzene–*n*-hexane (96%): mp 133.3–138.1° (K); ir (KBr) 1555, 1630 (C=O), and 3250 cm^{-1} (NH); nmr ($CDCl_3$) δ 5.96 (d, 1, $J \cong 8.7$ Hz, NH), 5.77 (m, 2, =CH), 4.41 (m, 1, W = 31 Hz, XCH), 3.22 (m, 1, W = 23.8 Hz, ArCH), 2.38 (s, 3, $ArCH_3$), 1.71 (s, 3, $COCH_3$).

Anal. Calcd for $C_{15}H_{19}NO$: C, 78.56; H, 8.35; N, 6.11. Found: C, 78.41; H, 8.18; N, 6.14.

Catalytic hydrogenation of compounds **4b**, **4d**, and **4e** utilizing 10% palladium on carbon in solutions of benzene or methanol afforded derivatives **5b**, **5d**, and **5e**.

trans-**2-***o*-**Tolylformamidocyclohexane** (**5b**) was recrystallized from benzene–*n*-hexane (98%): mp 129.2–130.0° (K); ir (KBr) 1550, 1660 (C=O), 2880 (formyl CH), and 3275 cm^{-1} (NH); nmr ($CDCl_3$) δ 7.70 (d, <1, J = 2 Hz, CHO, major), 7.42 (d, <1, J = 12.0 Hz, CHO, minor), 6.03 (m, <1, NH, major), 4.23 (m, <1, W > 30 Hz, XCH, major), ~3.33 (m, <1, XCH, minor), 2.75 (m, ~1, $W \cong 28$ Hz, ArCH), 2.31 (s, <3, $ArCH_3$, major), 2.23 (s, <3, $ArCH_3$, minor).

Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.44. Found: C, 77.10; H, 8.75; N, 6.53.

trans-**2-***o*-**Tolyl-***N*-**methylacetamidocyclohexane** (**5d**) was recrystallized from *n*-hexane–benzene (97%): mp 116.5–118.0° (K); ir (KBr) 1635 cm^{-1} (C=O); nmr ($CDCl_3$) δ 5.00 (m, <1, W > 25 Hz, XCH, major), ~3.93 (m, <1, XCH, minor), ~2.9 (m, ~1, ArCH), 2.63 (s, ≪3, NCH_3, minor), 2.57 (s, <3, NCH_3, major), 2.39 (s, ~3,[15] $ArCH_3$), 1.81 (s, ~3,[15] $COCH_3$), 2.09 (s, ≪3, either $ArCH_3$ or $COCH_3$ of minor conformer). Mass spectral analysis of the molecular ion gave m/e 245.1758 (calcd for $C_{16}H_{23}NO$: 245.1778).

Anal. Calcd for $C_{16}H_{23}NO$: C, 78.32; H, 9.45; N, 5.71. Found: C, 78.49; H, 9.00; N, 5.70.

trans-**2-***o*-**Tolylacetamidocyclohexane** (**5e**) was recrystallized from benzene–*n*-hexane (98%): mp 145.4–145.9° (K); ir (KBr) 1565, 1635 (C=O), and 3280 cm^{-1} (NH); nmr ($CDCl_3$) δ 5.81 (d, 1, J = 8.7 Hz, NH), 4.23 (m, 1, $W \sim 30$ Hz, XCH), 2.73 (m, 1, $W \sim 24$ Hz, ArCH), 2.33 (s, 3, $ArCH_3$), 1.62 (s, 3, $COCH_3$).

Anal. Calcd for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.06. Found: C, 77.90; H, 9.10; N, 6.05.

6,10-Dimethyl-4a,10b-*trans*-**1,2,3,4,4a,10b-hexahydrophenanthridine hydrochloride** (**6**) was prepared essentially as described by Whaley and Govindachari[6] for a general synthesis of phenanthridines by refluxing a solution of **5e**, phosphorus oxychloride (15 molar equiv excess), and dry chlorobenzene for 4 hr. The basified extract yielded the oil of the imine [ir (neat) 1635 cm^{-1} (C=N)], which was then treated with dry hydrogen chloride gas in benzene and recrystallized from 2-propanol to afford the salt in 29% yield: mp 222.8–225.8° (TH, sealed capillary); ir (KBr) 1665 (C=N), 2680 cm^{-1} (NH); nmr ($CDCl_3$) δ 7.59 (m, 3, aromatic), 3.06 (d, 3, J = 1.5 Hz, C-6 methyl), 2.61 (s, 3, C-10 methyl); free imine nmr ($CDCl_3$) δ 7.16 (m, 3, aromatic), 2.30 (d, 3, J = 1.5 Hz, C-6 methyl), and 2.43 (s, 3, C-10 methyl).

Anal. Calcd for $C_{15}H_{20}ClN$: C, 72.13; H, 8.07; N, 5.61. Found: C, 72.33; H, 8.05; N, 5.49.

Registry No.—**1a**, 34805-94-2; **1b**, 34805-95-3; **1c**, 34805-96-4; **1d**, 34805-97-5; **1e**, 34805-98-6; **2a**, 34805-99-7; **2b**, 34806-00-3; **3a**, 34806-01-4; **3b**, 34806-02-5; **3c**, 34806-03-6; **3d**, 34806-04-7; **4a**, 34806-05-8; **4b**, 34806-06-9; **4c**, 34806-07-0; **4d**, 34806-08-1; **4e**, 34806-09-2; **5b**, 34806-10-5; **5c**, 34806-11-6; **5d**, 34806-12-7; **5e**, 34806-13-8; **6**, 34806-14-9.

Acknowledgment.—We wish to thank Mr. Bernard J. Nist for the determination of the high-temperature nmr spectra.

(15) Because these signals overlap signals of the ring methylene hydrogens the integration does not allow the assignment of the minor CH_3 signal, at δ 2.13, to the $ArCH_3$ or $COCH_3$ signals.