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BENZO- AND INDOLOQUINOLIZINE DERIVATIVES—XVII

THE SYNTHESIS OF THE 1,2,3,4a,6,7,8,9,13b-DECAHYDRO-9aH-PYRIDO[1,2-f]PHENANTRIDINE ISOMERS

G. LAUS and G. VAN BINST*
Vrije Universiteit Brussel, Laboratorium voor Organische Chemie, Pleinlaan 2, B-1050 Brussel, Belgium

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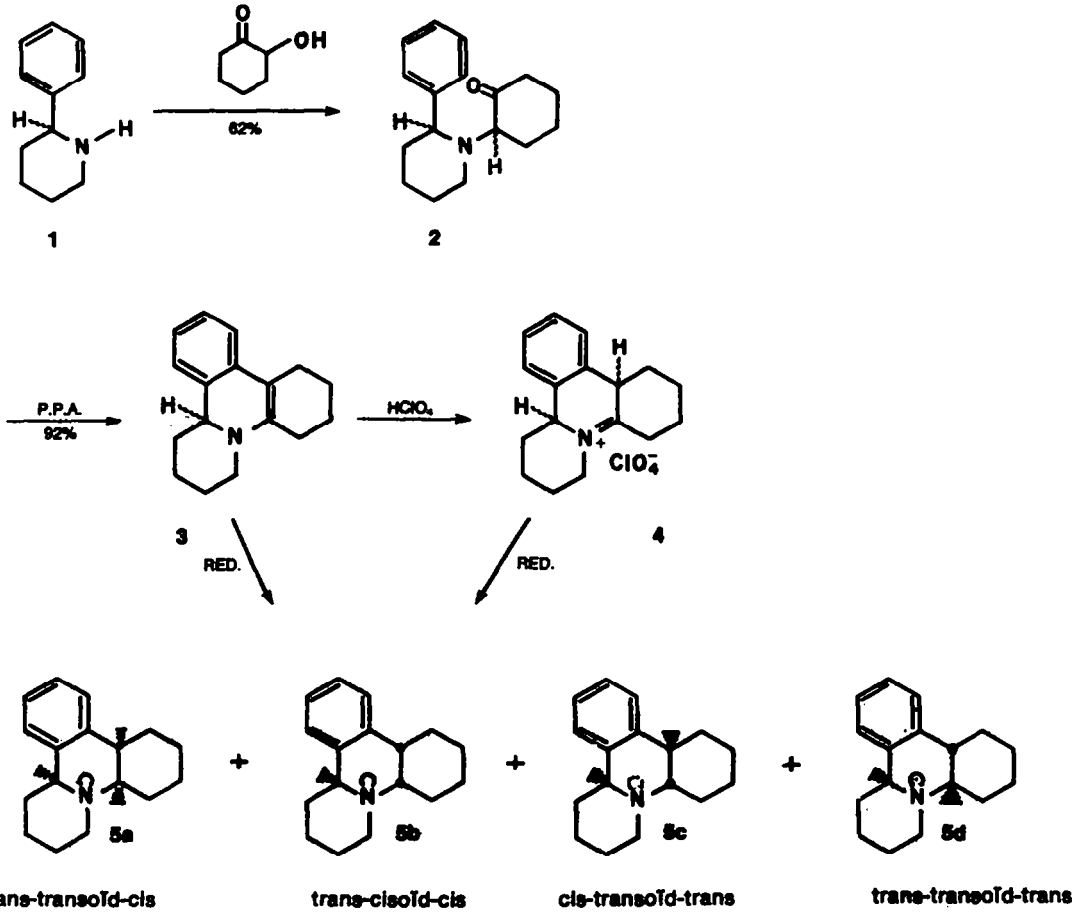
Abstract—The four possible diastereoisomers of 1,2,3,4a,6,7,8,9,13b - decahydro - 9aH - pyrido[1,2 - f]phenantridine were obtained by reduction of the enamine 1,2,3,4,6,7,8,9 - octahydro - 9aH - pyrido[1,2 - f]phenantridine or of its corresponding iminiumsalt. We report also the synthesis of two isomers of the title compound starting from trans-2-phenyl-cyclohexylamine.

1 *Reaction scheme*

The enamine 3 was prepared according to Scheme 1. Reduction of 2-phenylpyridine[2] yielded to 2-phenyl-piperidine[3] 1. Condensation of 1 with 2-hydroxycyclo-hexanone[4] gave 2-phenyl-N-(2-oxocyclohexyl)-piperi-dine 2, which was cyclized in polyphosphoric acid to the enamine 3.

2 *Reduction of enamine 3 and its iminium salt 4*

The reduction of enamine 3 and on its corresponding iminium salt 4 are summarized in Tables 1 and 2 respectively. The isomeric composition (Scheme 1) was determined by glc. The stereochemistry of the isomers was determined by ^1H and ^{13}C NMR spectroscopy as described.[5,6]



Scheme 1.

Table 1. Reduction of enamine 3

Reduction method	Total yield*	% isomers [5a]	[5b]	[5c]	[5d]
- H_2, PtO_2 3 h, 3% PtO_2	90	79	16	0	5
1 week, 100 % PtO_2	90	15	80	0	5
- $NaBH_4$/AcOH (or $NaBD_4$/AcOH)	80	52	27	0	21
- $AlHCl_2$	70	64	15	0	21
- B_2H_6	68	35	33	0	32
- Li/NH_3	83	21	12	34	33
- K-tri-sec-butyl-borohydride	-+	100	0	0	0
- HCOOH§ (or DCOOH, HCOOD)	40	95	5	0	0

* total yield : yield of the reactions after column chromatography on alumina basic Typ E (Merck) ; eluent : iso-octane and gradually iso-octane/ether mixtures.

\+ reaction only performed on small amounts to determine the relative yields of isomers by gas-liquid chromatography.

§ total yield and isomeric composition determined after column chromatography (many by-products in gas-liquid chromatogram).

Table 2. Reductions of iminium salt 4

Reduction method	Total yield*	% isomers [5a]	[5b]	[5c]	[5d]
- H_2, PtO_2 3 h, 3%PtO_2	-+	71	17	0	12
- $NaBH_4$ (or $NaBD_4$)	-+	71	15	0	10
- $LiAlH_4$ (or $LiAlD_4$)	60	71	18	0	11
- $LiAlH(O\text{-}t\text{-}but)_3$	-+	79	19	0	2
- K-tri-sec-butyl-borohydride	-+	100	0	0	0

3 *Discussion of the reduction reactions*

Stereochemistry of enamine 3 and its iminium salt 4. The reductions of 3 and 4 depend primarily on the stereochemistry of the starting material. The spatial arrangement of these structures was determined by ^1H NMR analysis.

Enamine 3. There are three possible conformers having chair- or half-chair rings: *trans* **6**, *cis*-1 **7** and *cis*-2 **8**. (Scheme 2).

The NMR-data of the spectrum of enamine 3 in deuterated chloroform are summarized in Table 3.

The low-field position of H9a (4.27 ppm), its axial position in ring A ($J_{9a,8ax.} = 11.5$ Hz, $J_{9a,8eq.} = 2.5$ Hz), and the close similarity of the spectrum of 3 with that of the *cis*-transoid-*trans* 5c[2] conformer prove that 3 exists mainly in the *cis*-2 **8** conformation. Only the structure with the double bond between C4a and C13b was detected in the spectrum.

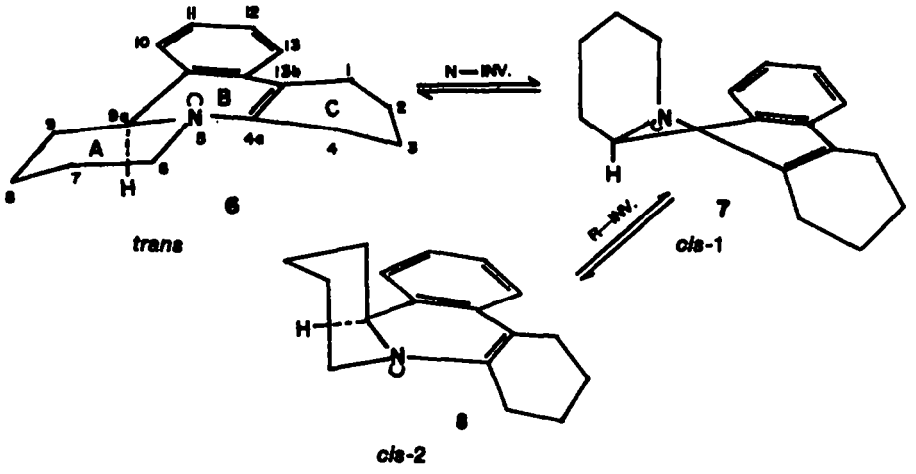
Iminium salt 4 (*perchlorate*). Two possible configurations, **9** and **10**, are considered for the iminium salt 4: (Scheme 3).

The perchlorate of the enamine 3 exists only under form 4 with the double bond between C4a and the N-atom. The ^1H NMR spectrum (Table 4) in trifluoroacetic acid shows a unique configuration but doesn't allow the distinction between structures **9** and **10** as the 9a and 13b H's are axial in respectively rings A and C in both structures.

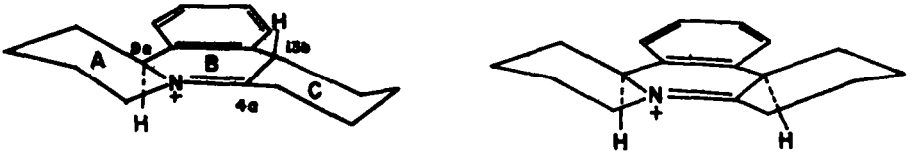
Dreiding models revealed that steric hindrance is equivalent for both the α- and β-side in molecule **9**, but that the β-side in molecule **10** shows much more steric interactions (crowding of rings A and C on the β-side) in comparison with the α-side. The reductions of 4 proved that the iminium salt exists as configuration **10** (see later).

The iminium salt formed in the acid medium (^1H NMR spectrum of 3 in deuterated acetic acid) showed an NMR spectrum identical with the isolated perchlorate (4).

Catalytic reduction. The catalytic hydrogenation of 3 after complete reduction (3 hr for 3% platinum(IV)-oxide at 4 atm hydrogen; 15 min for 100% platinum(IV)-oxide at 4 atm hydrogen) gave an excess of *trans*-transoid-*cis* isomer **5a** (79%). This result is consistent with the con-



Scheme 2.



Scheme 3.

Table 3. ^{1}H NMR-data of enamine 3 in $CDCl_3$

Proton	δ (ppm)	J (Hz)
H9a	4.27	$J_{9a,8ax.}$ = 11,5 Hz
		$J_{9a,8eq.}$ = 2,5 Hz
H6eq.	3.78	$J_{gem.}$ = - 14 Hz
		$J_{6eq.,7eq.}$ = 5 Hz
		$J_{6eq.,7ax.}$ = 3 Hz
H6ax.	2.78	$J_{gem.}$ = - 14 Hz
		$J_{6ax.,7ax.}$ = 11 Hz
		$J_{6ax.,7eq.}$ = 4 Hz
Other protons	2.36-1.25	

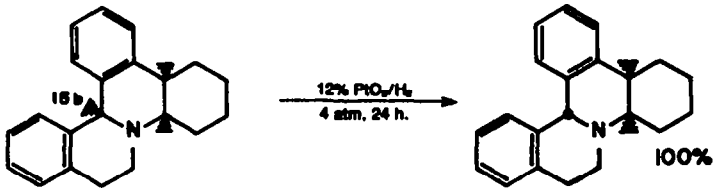
Table 4. ^{1}H NMR-data of iminium salt 4 in CF_3COOD

Proton	δ (ppm)	J (Hz)*
H9a	5.11	$J_{9a,8ax.}$ = ± 12
H6eq.	4.92	$J_{gem.}$ = ± (-13)
H13b	4.15	$J_{13b,1ax.}$ = -12
		$J_{13b,1eq.}$ = ± 5
H6ax.	3.83	

* The signals are broadened which prevents exact determination of the coupling constants.

formation 8 of the enamine (preferential hydrogenation on the α-side) and the mechanism of catalytic reduction of a double bond.[7]

As a function of time, 5a isomerised to 5b. Isomerisation from the kinetically formed isomer to the thermodynamic most stable isomer was also observed in an analogous series by Baert[4] (Scheme 4).



11 12

Scheme 4.

After one week under isomerisation conditions we obtained 15% of 5a and 80% of 5b. The nature of the isomerisation products and the large difference in reaction rate in both cases (5a: 1 week, and 11: 24 hr) proved that isomerisation occurs at H9a (5a) and H15b (11). An isomerisation study in protoberberines by Kametani[8] confirms this hypothesis.

No isomerisation was observed on a Pd-C catalyst. Catalytic reduction of the iminium salt 4 yielded again the *trans*-transoïd-*cis* 5a isomer, which proved the configuration 10 for the iminium salt by attack on the less hindered side.

Hydride reductions. The reduction of 3 with sodium borohydride-acetic acid and formic acid proceeded first by addition of a proton (from acetic acid or formic acid) to the β-position of 3. The salt thus formed was further reduced by attack of a hydride or hydride-transporting particle.[9,10]

The stereochemical implications of this reduction are summarized by Brown:[11] axial attack of the hydride on ring systems with little steric hindrance; attack from the less hindered side on ring systems with high steric interactions.

The excess of structure 5a in these reactions is consistent with hydride attack on the less hindered α-side of structure 10, which is formed in the acid medium (see above).

The reduction of the iminium salt 4 also yielded an excess of the *trans*-transoïd-*cis* isomer 5a by hydride addition on the iminium double bond from the steric most favourable side of structure 10.

A relatively important quantity of isomers 5a and 5d was formed during these hydride reductions. These isomers were obtained from structure 9 of the iminium salt or iminium intermediate. This is only possible if an equilibrium exists between structures 9 and 10 in ether or tetrahydrofuran. Reduction of 9 gave isomers 5b and 5d.

Because of the strong steric interactions on the β-side of structure 10 no *cis*-transoïd-*trans* isomer 5c was detected in these reactions.

A higher stereoselectivity occurs in the reduction of 4 with the bulkier lithium tri-t-butoxyaluminiumhydride.[12] With the very selective potassium tri-sec-butylborohydride[13] only isomer 5a was present in the mixture. Even 3 was reduced stereoselectively (100% of 5a) with potassium tri-sec-butylborohydride without addition of a proton-donor. The mechanism of this reduction of 3 is not clear.

The reaction conditions in the sodium borohydride reduction (sodium borohydride in tetrahydrofuran with gradually addition of acetic acid for reduction of 3 and sodium borohydride in tetrahydrofuran for reduction of 4) yielded a somewhat different isomeric composition. No isomerisation of 5 was detected under the conditions. The nature of the participation of the protonation source on the reaction components needs further investigation.

Aluminium dichlorohydride and diborane reductions. Aluminium dichlorohydride and diborane react on enamine 3 as Lewis acids and add as a proton on the β-carbon of the enamine structure[14,15] (Scheme 5).

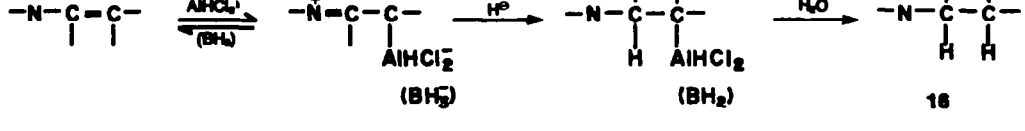
The stereochemical implications depends on the structure of intermediate 14, but due to lack of information we were not able to rationalize the results of these reductions. The bulkier aluminium dichlorohydride showed somewhat greater selectivity. No trace of isomer 5c was detected in the reaction.

Birch (lithium/ammonia) reduction. In this reduction of 3, which proceeds by electron addition and formation of anions and dianions,[16] the presence of the benzene ring which probably stabilizes the intermediates, is necessary. Reduction of 17 (Scheme 6) with lithium/ammonia was not accomplished.

Addition of the proton source at the end of the reaction led to an isomeric distribution, which reflected the thermodynamic stability of the anion intermediates. In this reduction we obtained for the first time the *cis*-transoïd-*trans* 5c isomer.

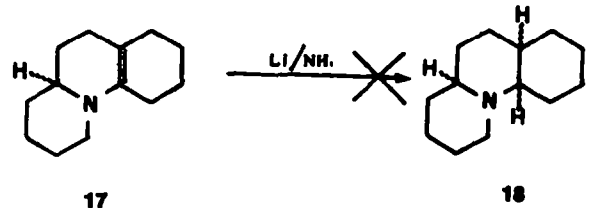
4 Synthesis of the title compound 5 from reactants with fixed stereochemistry

Starting from *trans*-2-phenylcyclohexylamine 19 we were able to synthesize isomers 5c and 5d in a



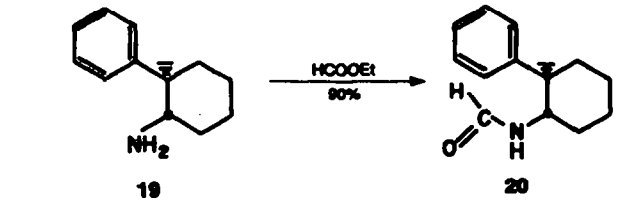
13 14 15 16

Scheme 5.

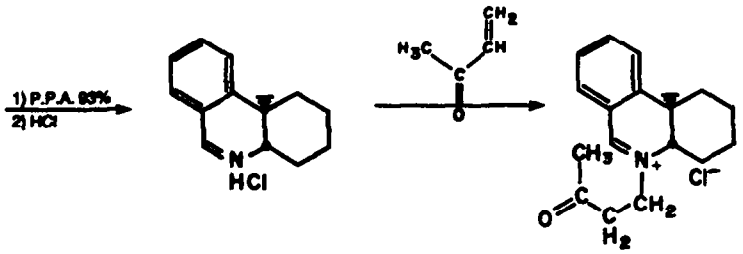


17 18

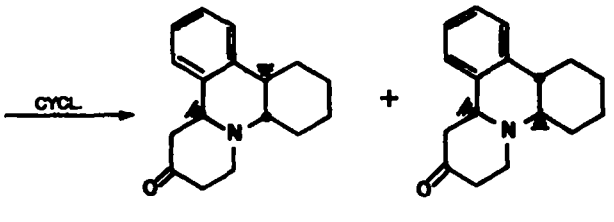
Scheme 6.



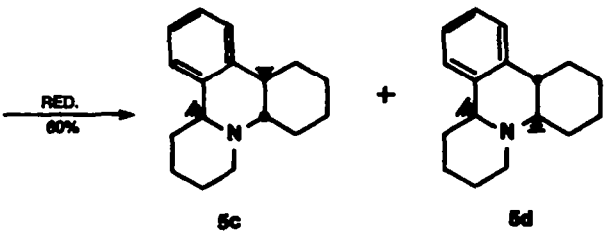
19 20



21 22



23 24



5c 5d

Scheme 7.

stereoselective way according to Scheme 7. The cyclization of the methylvinyl ketone addition product 22 was first attempted under basic conditions (10% NaOH). The overall yield of cyclized product was very low (20–30%). Only the *cis*-transoïd-*trans* isomer 23 was isolated. The cyclization of 22 on an aluminium oxide (Akt I) column with dichloromethane as eluent was quantitative. Here we obtained an isomer mixture *trans*-transoïd-*trans*/*cis*-transoïd-*trans*: 80/20.

CONCLUSION

We were able to synthesize the four possible diastereoisomers of 1,2,3,4a,6,7,8,9,13b - decahydro - 9aH - pyrido[1,2 - f]phenantridine according to Scheme 1 by reduction of the enamine 3 and its corresponding iminium salt 4. The reduction results were analyzed on the basis of the stereochemistry of structures 3 and 4. An alternative scheme (Scheme 7), in which the stereochemistry was partially fixed, was worked out for *cis*-transoïd-*trans* 5c and *trans*-transoïd-*trans* 5d isomers.

EXPERIMENTAL

2-Phenyl-N-(2-oxocyclohexyl)-piperidine 2. A mixture of 2-phenylpiperidine[3] (19.60 g, 0.122 mole) and 2-hydroxy-cyclohexanone[21] (14 g, 0.122 mole) in toluene was refluxed in a Dean and Stark apparatus until no further separation of water was obser-

ved (45 hr). After evaporation of the solvent, the crude product was distilled (b.p. 154–156°/2 mm), yield 62%. Recrystallisation from EtOH or petroleum ether 40/60 gave crystals, m.p. 82–84°; IR spectrum (C_2Cl_4): ν_{CO}: 1715 cm^{-1}; MS: $M^{+\cdot}$ peak: 257, base peak: 91; PMR spectrum (C_6D_6): δ (ppm): 4.43 (H1), 3.39 (H5ax), 3.10 (H11), 2.96 (H5eq), 2.0 (H12eq), 1.04 (H12ax).

1,2,3,4,6,7,8,9 - Octahydro - 9aH - pyrido[1,2 - f]phenantridine (3). Compound 2 (5.10 g, 0.02 mole) was heated with polyphosphoric acid (50 g) at 125–130° under vigorous stirring for 1.5 hr. The cold mixture was poured onto ice and the soln was made basic with NaOH pellets. After extraction with ether, drying over $MgSO_4$ and evaporation of the solvent, the residue was distilled (b.p. 182–186°/0.9 mm), yield: 92%; IR spectrum (C_2Cl_4): enamine band: 1615 cm^{-1}; MS: $M^{+\cdot}$ peak: 239, base peak: 183; PMR spectrum ($CDCl_3$): δ (ppm): 4.27 (H9a), 3.78 (H6eq), 2.78 (H6ax); picrate: m.p.: 191–193°, perchlorate 4: m.p.: 205–210°.

Catalytic hydrogenation. Enamine 3 (1.0 g, 0.0042 mole) dissolved in abs EtOH (100 ml) was hydrogenated in a Parr apparatus at 4 atm H_2 over PtO_2 as catalyst. After filtration, the EtOH was evaporated and the hydrogenation products were chromatographed (alumina H basic type E Merck, eluent: iso-octane and gradually iso-octane/ether mixtures). Two well-separated fractions were collected and recrystallised from iso-octane, total yield: 90%.

Fraction 1: isomer 5a m.p.: 52–54% (79% of the mixture for 3 hr hydrogenation over 3% PtO_2; 15% for 1 week hydrogenation over 100% PtO_2), IR spectrum (CCl_4): Bohlmannbands: 2780 and 2740 cm^{-1} (intens); MS: $M^{+\cdot}$ and base peak: 241; PMR spectrum: see Ref. (5).

Fraction 2: isomer 5b m.p.: 81–82° (16% for 3 hr hydrogenation over 3% PtO_2, 80% for 1 week hydrogenation over 100% PtO_2). IR spectrum (CCl_4): Bohlmannbands: 2790 and 2750 cm^{-1} (weak); MS: $M^{+\cdot}$ peak and base peak: 241; PMR spectrum: see Ref. (5).

The same procedure for 4 gave 71% of 5a and 19% of 5b for 3 hr hydrogenation and 3% PtO_2.

Sodium borohydride reduction. To a stirred suspension of 3 (1.0 g, 0.0042 mole) and $NaBH_4$ (1.5 g, 0.04 mole) in freshly distilled THF (100 ml), AcOH (10 ml) was carefully added dropwise and the mixture was neutralized by addition of 10% NaOH aq. After extraction with ether, drying over $MgSO_4$ and evaporation of the ether, the mixture was chromatographed as described for the catalytic hydrogenation products. Three separated fractions were collected and recrystallised from iso-octane, total yield: 80%.

Fractions 1 and 2 were identical with fractions 1 and 2 respectively of the catalytic hydrogenation. (5a: 52%, 5b: 27%).

Fraction 3: isomer 5d: 21%, m.p.: 78–79°, IR spectrum: Bohlmannbands: 2780 and 2840 cm^{-1} (weak); MS: $M^{+\cdot}$ and base peak: 241; PMR spectrum: see Ref. (5).

The same procedure for 4 without addition of AcOH gave: 5a: 71%, 5b: 19%, 5d: 10%.

Aluminium dichloro hydride reduction. $AlHCl_2$[22] was prepared by addition of an ether soln of $AlCl_3$ (1.75 g, 0.015 mole) to a suspension of LAH (0.2 g, 0.005 mole) in ether. The enamine 3 (1.0 g, 0.0042 mole) in ether was dropped into the stirred suspension of $AlHCl_2$ and the mixture was refluxed for 2 hr under N_2. EtOAc was added to destroy the excess of $AlHCl_2$. The mixture was worked up in the usual manner (see $NaBH_4$ reduction), total yield: 70%; Isomers 5a: 64%, 5b: 15% and 5d: 21% were isolated.

Diborane reduction. Enamine 3 (1.0 g, 0.0042 mole) dissolved in freshly distilled THF (100 ml) was put into a 250 ml 3-necked, round bottom flask, equipped with a mechanical stirrer, diborane gas inlet and condensor. Diborane gas, prepared from $NaBH_4$ (5 g) and BF_3 etherate (20 ml) in ether was led into the vessel (kept at room temp.) for 1 hr. The mixture was then refluxed for 1 hr. AcOH was then added in excess and further refluxed for 2 hr. The soln was cooled and neutralized with $NaHCO_3$. The mixture was worked up in the usual manner, total yield: 69%; Isomer 5a: 35%, 5b: 33% and 5d: 33% were isolated.

Formic acid reduction. Enamine 3 (1.0 g, 0.0042 mole) was heated at 60° with formic acid (1 mol, 0.023 mole) for 3 hr. After cooling, the products were added to 10% NaOH aq (25 ml). The mixture was worked up in the usual manner, total yield: 40%; isomers 5a: 95% and 5b: 5% were isolated.

K-Tri-sec-butylborohydride reduction. Enamine 3 (100 mg, 0.00042 mole) in freshly distilled THF and K-tri-sec-butyl borohydride (0.5 g, 0.002 M) was stirred for 15 hr at room temp. Water was added and most of the THF was evaporated. The reaction was worked up in the usual manner, followed by an acid-base extraction.

The products were analyzed only by glc (100% of 5a). The same result was obtained for a reduction at −60°. The same procedure for 4 gave the same result.

Lithium/ammonia reduction (Birch reduction). Enamine 3 (1.0 g, 0.0042 mole) dissolved in a minimum of dry ether was slowly added to a stirred soln of Li (0.2 g, 0.028 mole) in liquid ammonia (300 ml) and stirred for 5 hr. After addition of an excess of NH_4Cl, the ammonia was allowed to evaporate.

After addition of water, the reaction was worked up in the usual manner, total yield: 83%. Four fractions were isolated after column chromatography.

Fractions 1, 2 and 4 are identified as 5a: 21%, 5b: 12% and 5d: 33%.

Fraction 3: isomer 5c: 34%, m.p. 58–60°; IR spectrum (CCl_4): no Bohlmann bands; MS: $M^{+\cdot}$ and base peak: 241; PMR spectrum: see Ref. (5).

Lithium aluminium hydride reduction. The perchlorate salt 4 (1.0 g, 0.004 mole) and LAH (1.160 g, 0.04 mole were suspended in dry, freshly distilled THF (100 ml) and refluxed for 4 hr. After cooling the mixture, water (10 ml) was carefully added, followed by addition of 10% NaOH aq (10 ml). The reaction was worked up in the usual manner, total yield: 60%; isomers 5a: 71%, 5b: 18% and 5d: 11% were isolated.

Lithium tri-t-butoxyaluminiumhydride reduction.[23] Same procedure as for the LAH reduction on 100 mg of 4. The products were analyzed only by glc: 5a: 79%, 5b: 19% and 5d: 2%.

1,2,3,4,4a,6,7,8,9,13b - Decahydro - trans - 9aH - pyrido[1,2 - f]phenantridine derivatives 23 and 24. *Trans-2-Phenylcyclohexylamine* 19.[17] *trans-1-formylamino-2-phenylcyclohexane* 20 and *trans-1,2,3,4,4a,10b hexahydrophenantridine hydrochloride* 21 were prepared as described.[18]

Compound 21 (1 g, 0.0045 mole) and an excess methyl vinyl ketone (15 ml) were heated at 60–70° for 1 hr. Methyl vinyl ketone was evaporated.[19]

(a) The crude product 22 was added to a 10% NaOH aq and stirred for 1 hr. After extraction with ether, drying over $MgSO_4$ and evaporation of the solvent, the mixture was purified on column (alumina Act I, eluent: ether), yield: 20–30% of product 23.

Recrystallisation from petroleum ether 40/60 gave crystals: m.p. 145–146°; IR spectrum (KBr): ν_{CO}: 1705 cm^{-1}; MS: $M^{+\cdot}$ peak: 255, base peak: 212; PMR spectrum ($CDCl_3$): δ (ppm): 4.31 (H9a), 3.73 (H6eq), 3.00 (H6ax).

(b) The cyclization of 22 was performed by pouring the product over an alumina column Act I with dichloromethane as eluent; yield: 90%.

The product was an isomer mixture 23/24 = 20/80, which could not be separated completely; PMR spectrum of 24: ($CDCl_3$): δ (ppm): 3.83 (H9a), 3.74 (H6eq).

Huang–Minlon reduction of 23 *and* 24.[20] Product 23 (1.0 g, 0.004 mole) or the mixture 23 and 24 (1 g, 0.004 mole) were heated for 4 hr with hydrazine hydrate (4 ml) and KOH (3 g) in ethylene glycol (30 ml) at 160°. After cooling, water was added. The product was extracted with ether, the ether soln was washed with water, dried over Na_2SO_3 and the ether evaporated. The resulting crude product was purified on an alumina column Act I with benzene as eluent, yield: 60% of 5c or of a mixture (5c and 5d.

The NMR spectra were recorded on a Bruker HX 270 pulsed-Fourier-spectrometer. The IR spectra were recorded on a Perkin-Elmer 257 spectrometer. The mass spectra were recorded on a A.E.I. MS902S apparatus. The gas-liquid chromatography was performed on a Varian Aerograph 1520-B apparatus.

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