SYNTHESIS AND CONFORMATIONAL ANALYSIS OF *cis*-3a-(*o*-NITROPHENYL)OCTAHYDROINDOL-4-OL DERIVATIVES

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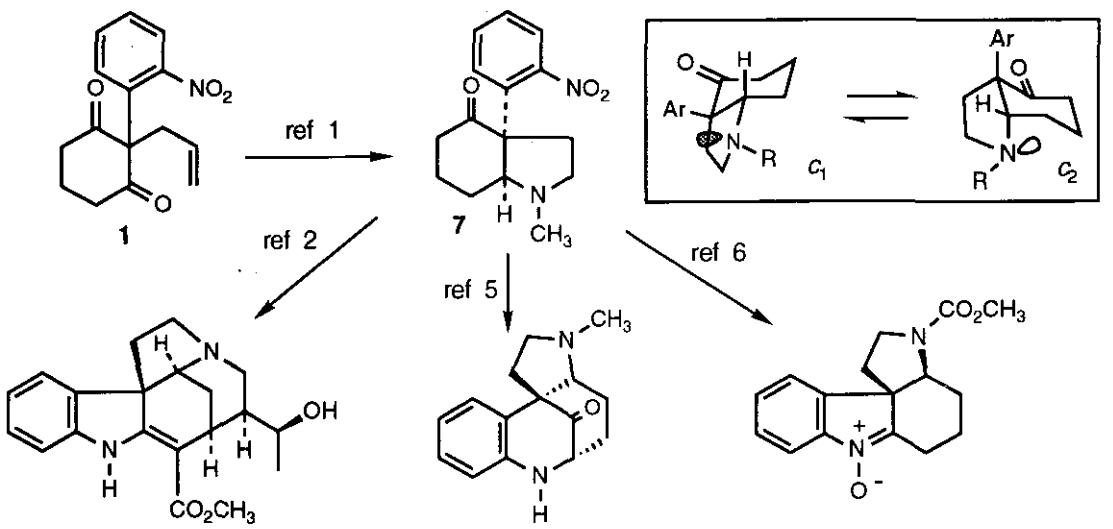
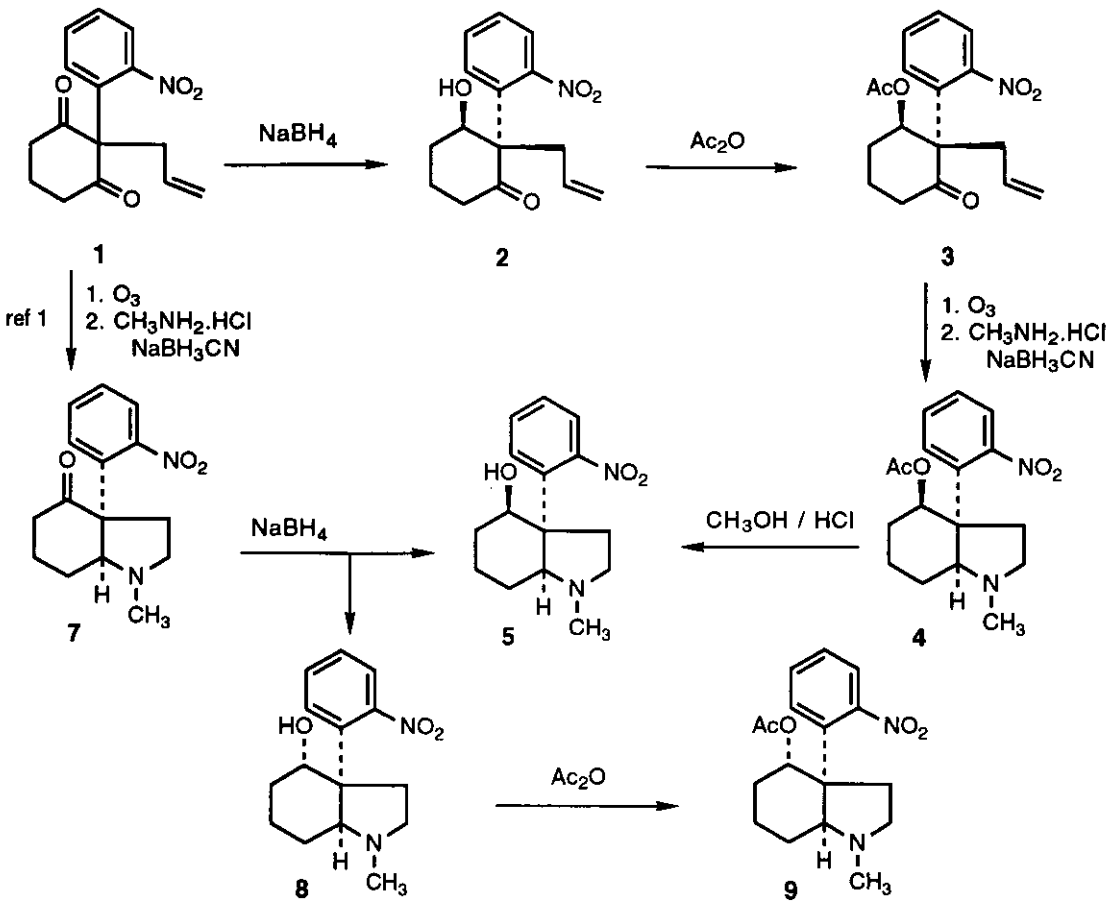
Abstract - The preparation of 1-methyl-3a-(*o*-nitrophenyl)octahydroindol-4-ol derivatives from 2-allyl-2-(*o*-nitrophenyl)-1,3-cyclohexanedione (**1**) and the preferred conformation of the azabicyclic ring system of these compounds are reported.

We have recently described the synthesis of 3a-(*o*-nitrophenyl)octahydroindol-4-ones (*e.g.* **7**) by a process involving the double reductive amination of a γ-keto aldehyde generated *in situ* by reductive ozonolysis of 2-allyl-2-(*o*-nitrophenyl)-1,3-cyclohexanedione (**1**).[1] These azabicyclic derivatives have shown to be valuable precursors of *Strychnos* indole alkaloids[2-4] and related heterocyclic systems.[5,6] Interestingly, *cis*-3a-(*o*-nitrophenyl)octahydroindol-4-ones show a peculiar conformational behavior, changing their preferred conformation, c_1 *vs* c_2 (c_1 and c_2 refer to the *N*-outside and *N*-inside conformers, respectively) depending on the substituent linked at the nitrogen atom.[1b]



Scheme 1



Scheme 2. Synthesis of *cis*-1-methyl-3a-(*o*-nitrophenyl)octahydroindol-4-ol derivatives

In order to gain more knowledge of the conformational behavior of 3a-(*o*-nitrophenyl)octahydroindoles, we decided to prepare some octahydroindol-4-ol derivatives. With this aim, in this paper we describe the synthesis of alcohols (**5**) and (**8**) and acetates (**4**) and (**9**), and study the preferred conformation of these compounds on the basis of their spectroscopic data.

Results

The title compounds were prepared from 2-allyl-2-(*o*-nitrophenyl)-1,3-cyclohexanedione (**1**),[1] as shown in Scheme 2. The reduction of dione (**1**) with $NaBH_4$ was stereoselective,[7] affording alcohol (**2**) in 76% yield.[8,9] Attempts to generate the octahydroindole nucleus from ketol (**2**), following the methodology previously developed for the synthesis of 3a-(*o*-nitrophenyl)octahydroindol-4-ones, were unsuccessful, since the intermediate aldehyde coming from the degradation of the allyl side chain formed a stable hemiacetal with the free hydroxyl group. When the alcohol (**2**) was protected as an acetate, the ozonolysis-double reductive amination process afforded the octahydroindole nucleus in a stereoselective manner, the *cis*-octahydroindole (**4**) being the sole product obtained in

the reaction. The stereoselective formation of **4** starting from acetate (**3**) is worthy of mention because, under the same conditions, cyclohexanedione (**1**) affords an 1.5:1 mixture of **7** and its *trans* derivative, respectively.[1] The stereochemical course of the iminium salt reduction to provide **4** can be rationalized by assuming that the hydride attack takes place through an intermediate with the conformation **A**, in which the C(4) acetoxy substituent is in the equatorial orientation (*vide infra* for the conformational analysis of **4**).[10]

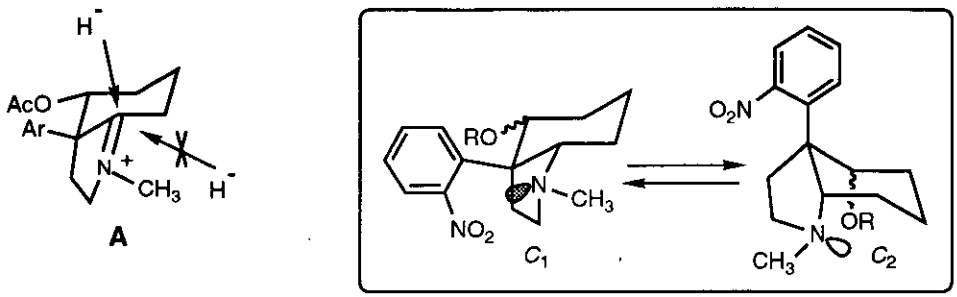


Figure 1

The methanolysis of acetate (**4**) provided alcohol (**5**). The epimeric alcohol (**8**) was prepared by reduction of ketone (**7**). This reduction gave a 5:3 mixture of alcohols (**8**) and (**5**). Acetylation of alcohol (**8**) afforded acetate (**9**). Both processes occurred in low yields, presumably due to the steric crowding exerted at C-4 by the adjacent quaternary carbon.

Conformational analysis

The first studies on the conformational behavior of *cis*-3a-arylhydroindoles were done by Jeffs,[11] who concluded that mesembranol, 6-epimesembranol and their corresponding acetates preferentially adopt a conformation that places the aryl group axially and the angular H_{7a} hydrogen in an equatorial disposition with respect to the cyclohexane ring (c_2 conformation type). The same conclusion was established by Stevens for the deeply related *Sceletium* alkaloids (*e.g.* mesembrine).[12] Finally, in a series of *cis*-3a-aryloctahydroindol-4-ones synthesized by Overman[13] as intermediates in the synthesis of *Amaryllidaceae* alkaloids, all compounds also showed a preferred c_2 type conformation.[14]

In our recent work about *cis*-3a-(*o*-nitrophenyl)octahydroindol-4-ones we demonstrated that in some cases the conformation c_1 is the preferred one for these compounds, and we described for the first time *cis*-3a-aryloctahydroindoles that place the aryl group in an equatorial disposition.[1b]

In the series of derivatives (**4**), (**5**), (**8**), and (**9**), here synthesized, a new compound with the unusual conformational preference for c_1 was found. Thus, whereas compounds (**5**), (**8**), and (**9**) exhibit an excellent correlation of their ^{13}C NMR data with respect to those of the reference ketone (**7**),[15] acetate (**4**) clearly shows a different ^{13}C NMR pattern, which suggests the conformational change (see Figures 1 and 2).

The most significant differences in the ^{13}C NMR data for **4** and **5**, which corroborate that these compounds differ in the conformation of the heterocyclic ring, are the chemical shifts of *C*-3 (δ 28.9 for **4** and δ 34.1 for **5**) and *C*-6 (δ 18.2 for **4** and δ 13.1 for **5**). The existence of a 1,3-diaxial relationship involving the substituent at C-4 explains the upfield shift observed in both cases. The preferred conformation for alcohol (**5**) with the axially located hydroxyl group can be accounted for by considering the existence of an intramolecular hydrogen bond of OH with the amino group. Indeed, the IR spectrum of **5** shows an OH absorption at 3309 cm^{-1} in CCl_4 solution which persists irrespective of its concentration.

The ^1H NMR data agree with a c_1 conformation for **4** and a c_2 conformation for **9**. The characteristic differences between the two spectra are: (i) The more deshielded H-2 proton[16] appears at a higher field in acetate (**4**) (δ 2.85) than in **9** (δ 3.1), owing to the shielding anisotropic effect of the benzene ring, only appreciable in the conformation c_1; (ii) the chemical shift of H-7a appears at a lower field in **4** (δ 3.16) than in **9** (δ 2.91) due to the proximity of the nitrogen lone pair; (iii) a coupling constant of 9 Hz for the H-4 proton, attributable to a trans diaxial relationship with an H-5 proton, only

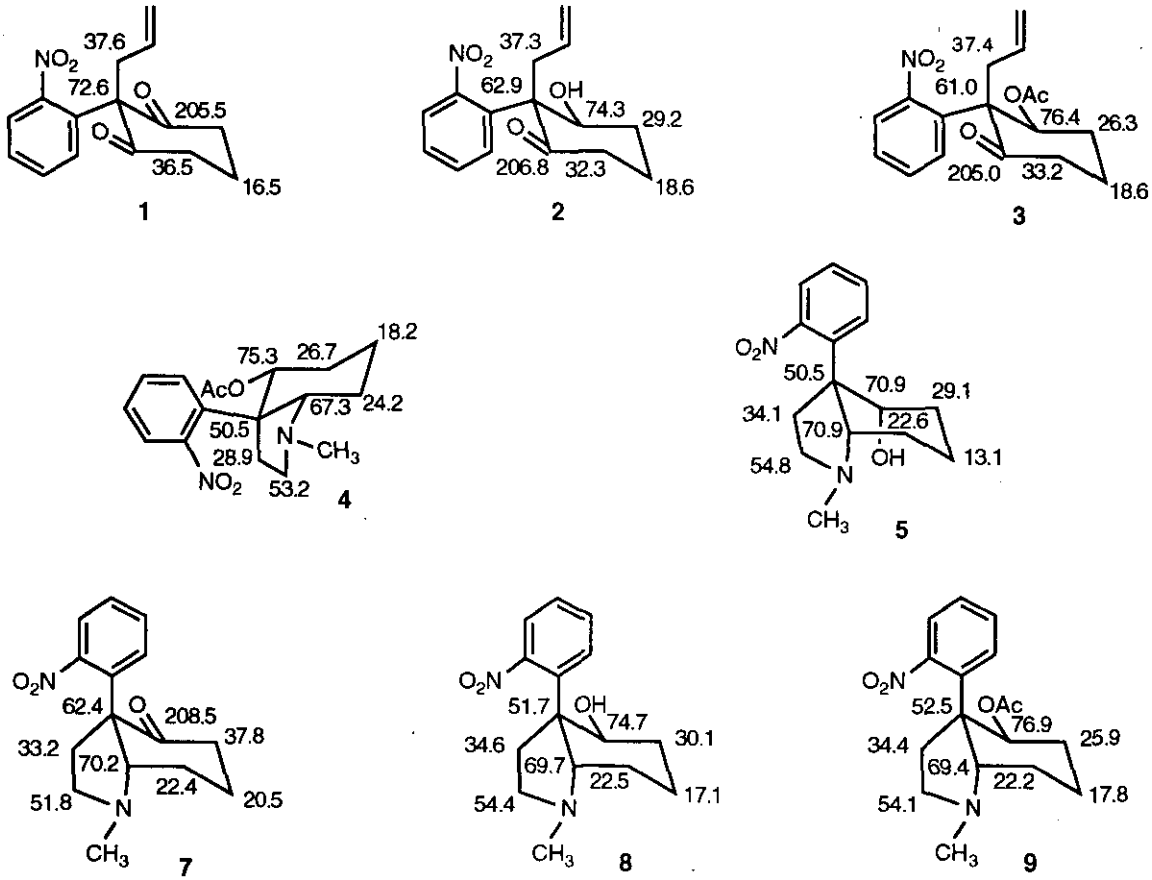


Figure 2. Selected ^{13}C NMR data of 1-5, 7-9 and their preferred conformations

possible in a conformation of type c_1 (the ring distortion that modifies the torsion angle in bicyclo[4.3.0]alkanes[17] and the electronegativity of the C-4 substituent[18] gives rise to the low value for this trans diaxial coupling constant). The coupling constant values for the H-7a in **4** can be attributed to a distortion of the carbocyclic ring that releases the 1,3-interaction of the *N*-methyl group and the C_7-H axial bond.

The conformation of cyclohexanone derivatives (**1**), (**2**), and (**3**) was inferred from the chemical shift of the methylene group of the allyl chain (δ 37 for an axial disposition).[9,19] Furthermore, in acetate (**3**) the coupling constant (J =11 Hz) of 3-H methine is indicative of a trans-diaxial relationship. The conformation of dione (**1**) is noteworthy since in simple 1-aryl-1-alkylcyclohexanes the aryl group lies in an axial disposition.[20]

In conclusion, the presence of a nitro group in the phenyl ring seems to be a contributive factor in the conformational behavior of 3a-aryloctahydroindoles and arylcyclohexane derivatives because related compounds with other substituents in the aromatic ring adopt a different conformation.[11,13]

EXPERIMENTAL

Unless otherwise noted, ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution at 300 and 75 MHz respectively, using TMS as an internal standard. Chemical shifts are reported in ppm downfield (δ) from TMS. IR spectra were recorded on a Nicolet 205 FT infrared spectrophotometer and the only noteworthy absorptions are listed (cm^{-1}). TLC was carried out on SiO_2 (silica gel 60 F_{254}, Merck), and the spots were located with iodoplatinate reagent. Chromatography refers to flash chromatography and was carried out on SiO_2 (silica gel 60, SDS, 230-400 mesh ASTM). Solvents were dried and purified prior to use when deemed necessary. Drying of organic extracts during workup of reactions was performed over anhydrous Na_2SO_4. Evaporation of solvents was accomplished with a rotatory evaporator. Microanalyses and HRMS were performed by the Centro de Investigación y Desarrollo (CSIC), Barcelona.

2-Allyl-*t*-3-hydroxy-*r*-2-(*o*-nitrophenyl)-1-cyclohexanone (2). To a solution of dione (**1**) (200 mg, 0.73 mmol) in THF (5 mL) was added an aqueous solution of $NaBH_4$ (9 mg, 0.22 mmol in 0.4 ml). After stirring the mixture at room temperature for 2 h, an additional portion of $NaBH_4$ (9 mg, 0.22 mmol) was added. After a 2 h period, an additional portion of $NaBH_4$ (9 mg, 0.22 mmol) was added. The mixture was stirred at room temperature for 1.5 h, poured into 5% aqueous HCl, and extracted with Et_2O. The combined organic extracts were washed with brine, dried, and evaporated to give a residue, which was purified by chromatography. Elution with 0.5:99.5 MeOH-CH_2Cl_2 gave ketol (**2**) (153 mg, 76%) as an oil: IR (film) 3617, 1703, 1528, 1358; ^{1}H NMR 1.85-2.10 (m, 4H), 2.36 (m, 2H), 2.55 (dd, J = 16.5, 7 Hz, 1H), 3.47 (dd, J = 16.5, 5.5 Hz, 1H), 4.58 (br, 1H), 4.85-5.35 (m, 3H), 7.38-7.55 (m, 3H), 7.86 (d, J = 8 Hz, 1H); ^{13}C NMR 18.6 (C-5), 29.2 (C-4), 32.3 (C-6), 37.3 (CH_2), 62.9 (C-2), 74.3 (C-3), 118.2 (=CH_2), 125.7 (C-3'), 127.8 (C-4'), 131.6 (C-6'), 132.1 (C-5'), 132.2 (=CH), 133.9 (C-1'), 149.5 (C-2'), 206.8 (C-1). HRMS Calcd for $C_{15}H_{17}NO_4$ 275.1153, found 275.1189.

***t*-3-Acetoxy-2-allyl-*r*-2-(*o*-nitrophenyl)-1-cyclohexanone (3).** To a solution of **2** (547 mg, 2 mmol) in pyridine (3.5 mL) was added acetic anhydride (1.2 mL, 12.6 mmol). After 16 h at room temperature, the excess of reagents were removed *in vacuo*. The residue was dissolved in CH_2Cl_2 and washed with 5% aqueous HCl and brine. The organic extract was dried and concentrated to give a residue. Chromatography (CH_2Cl_2) gave **3** (499 mg, 79%) as an oil: IR (film) 1743, 1699, 1527, 1375; ^{1}H NMR 1.90-2.30 (m, 4H), 1.96 (s, 3H, CH_3), 2.45 (m, 2H), 2.72 (dd, J = 16.3, 7.2 Hz, 1H), 3.45 (dd, J = 16.3, 5.8 Hz, 1H), 4.99 (ddt, J = 9.9, 1.9, 1.3 Hz, 1H, H-*trans*), 5.09 (ddt, J = 17, 1.9, 1.3 Hz, 1H, H-*cis*), 5.25-5.47 (m, 1H, =CH), 5.86 (dd, J = 11.2, 4.6 Hz, 1H, H-3_{ax}), 7.38-7.59 (m, 3H), 7.92 (dd, J = 8,1.5 Hz, 1H); ^{13}C NMR 18.6 (C-5), 20.8 (CH_3), 26.3 (C-4), 33.2 (C-6), 37.4 (CH_2), 61.0 (C-3), 76.4 (C-2), 118.5 (=CH_2), 126.0 (C-3'), 128.2 (C-4'), 130.6 (C-6'), 131.6 (C-5'), 132.2 (=CH), 133.1 (C-1'). 149.6 (C-2'), 169.3 (COO), 205.0 (C-1). *Anal.* Calcd for $C_{17}H_{19}NO_5$: C, 64.34; H, 6.03; N, 4.41. Found: C, 64.47; H, 6.13; N, 4.37.

(3a*RS*,4*RS*,7a*SR*)-4-Acetoxy-1-methyl-3a-(*o*-nitrophenyl)octahydroindole (4). A stirred solution of **3** (977 mg, 3.07 mmol) in CH_2Cl_2 (120 mL) at -78 °C was charged with a constant stream of ozone. When the solution turned a characteristic pale blue it was purged with oxygen. Me_2S (1.5 mL) was added and the stirring was continued for 1 h. The solvent was removed *in vacuo* and the residue was dissolved in MeOH (15 mL). To the solution were added first a solution of methylamine hydrochloride (827 mg, 12.25 mmol) in MeOH (10 mL) and then $NaBH_3CN$ (45 mg, 0.76 mmol). After 30 min of stirring, an additional portion of $NaBH_3CN$ (45 mg, 0.76 mmol) was added and the stirring was continued for 1 h. At this time, an additional portion of $NaBH_3CN$ (144 mg, 2.3 mmol) was added and the stirring was continued overnight. The solvent was removed under reduced pressure, and the residue was partitioned between CH_2Cl_2 and saturated aqueous K_2CO_3 solution. The combined organic extracts were dried and evaporated to give a residue, which was chromatographed. On elution with 10:90 MeOH-CH_2Cl_2 octahydroindole (**4**) (405 mg, 41%) was obtained as an oil: IR (film) 1737,1526,1361, 1242; ^{1}H NMR 1.38-1.63 (m, 3H), 1.72-1.95 (m, 3H), 1.93 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.36-2.48 (m, 2H), 2.59 (m, 1H), 2.85 (td, J = 8.5, 4 Hz, 1H, H-2_β), 3.16 (dd, J = 7.5, 5 Hz, 1H, H-7a), 5.72 (dd, J = 9, 5 Hz, 1H, H-4_{ax}), 7.35 (td, J = 8, 1.5 Hz, 1H), 7.48 (td, J = 8, 1.5 Hz, 1H), 7.54 (dd, J = 8, 1.5 Hz, 1H), 7.64 (dd, J = 8, 1.5 Hz, 1H); ^{13}C NMR 18.2 (C-6), 20.7 (CH_3), 24.2 (C-7), 26.7 (C-5), 28.9 (C-3), 39.6 (NCH_3), 50.5 (C-3a), 53.2 (C-2), 67.3 (C-7a), 75.3 (C-4), 125.4 (C-3'), 127.5 (C-4'), 129.3 (C-6'), 130.8 (C-5'), 136.9 (C-1'), 150.6 (C-2'), 169.2 (CO). *Anal.* Calcd for $C_{17}H_{22}N_2O_4 \cdot 1/2H_2O$: C, 62.37; H, 7.07; N, 8.55. Found: C, 62.43; H, 6.76; N, 8.58.

(3a*RS*,4*RS*,7a*SR*)-1-Methyl-3a-(*o*-nitrophenyl)octahydroindol-4-ol (5). A solution of **4** (169 mg, 0.53 mmol) in a methanolic solution of hydrogen chloride (1.12 N, 20 mL) was stirred at room temperature overnight. The solvent was evaporated, the residue was dissolved in CH_2Cl_2 and washed with saturated aqueous Na_2CO_3 solution. The organic extracts were dried and evaporated to give a residue. Chromatography (3:97 MeOH-CH_2Cl_2) gave **5** (96 mg, 65%) as an amorphous solid: mp 114-116 °C (1:1 Et_2O-hexane); IR (KBr) 1529,1364; (CCl_4) 3309, 1534, 1365; ^{1}H NMR 1.10-1.38 (m, 2H), 1.62-2.04 (m, 5H), 2.19 (m, 1H), 2.27 (s, 3H, NCH_3), 2.75 (m, 2H), 3.17 (td, J = 9.5, 2.8 Hz, 1H, H-2_α), 4.07 (dd, J = 4, 1.5 Hz, 1H, H-4_{eq}), 7.32-7.52 (m, 4H); ^{13}C NMR 13.1 (C-6), 22.6 (C-7), 29.1 (C-5), 34.1 (C-3), 39.3

(NCH_3), 50.5 (C-3a), 54.8 (C-2), 67.8 (C-7a), 70.9 (C-4), 125.2 (C-3'), 127.4 (C-4'), 128.8 (C-6'), 131.0 (C-5'), 136.7 (C-1'), 151.7 (C-2'). *Anal.* Calcd for $C_{15}H_{20}N_2O_3$: C, 65.19; H, 7.29; N, 10.13. Found: C, 65.11; H, 7.36; N, 10.11.

(3a*RS*,4*SR*,7a*SR*)-1-Methyl-3a-(*o*-nitrophenyl)octahydroindol-4-ol (8). To a solution of **7**[1] (100 mg, 0.36 mmol) in EtOH (10 mL) cooled to -20 °C was added $NaBH_4$ (83 mg, 2.2 mmol). The mixture was stirred overnight and then quenched with 3 N aqueous HCl solution (10 mL). The solvent was removed *in vacuo*, the resulting residue was basified with saturated aqueous $NaHCO_3$ solution and extracted with CH_2Cl_2. The organic extracts were dried and concentrated to give a residue. Chromatography (from CH_2Cl_2 to 5:95 MeOH-CH_2Cl_2) afforded alcohol (**5**) (12 mg, 13%) as an amorphous solid and alcohol (**8**) (22 mg, 23%) as an oil. Compound (**8**): IR (film) 1529, 1365; ^{1}H NMR 1.35-2.30 (m, 9H), 2.25 (s, 3H, NCH_3), 2.77 (t, J = 3.5 Hz, 1H, H-7a), 3.09 (td, J = 8, 2.5 Hz, 1H, H-2$_\alpha$), 4.21 (dd, J = 8.2, 3.2 Hz, 1H, H-4$_{ax}$), 7.35-7.75 (m, 4H); ^{13}C NMR 17.1 (C-6), 22.5 (C-7), 30.1 (C-5), 34.6 (C-3), 39.9 (NCH_3), 51.7 (C-3a), 54.4 (C-2), 69.7 (C-7a), 74.6 (C-4), 125.4 (C-3'), 127.4 (C-4'), 130.9 (C-6'), 131.4 (C-5'); HRMS Calcd for $C_{15}H_{21}N_2O_3$ 277.1566, found 277.1552.

(3a*RS*,4*SR*,7a*SR*)-4-Acetoxy-1-methyl-3a-(*o*-nitrophenyl)octahydroindole (9). A solution of **8** (28 mg, 0.09 mmol) in pyridine (1 mL) was treated with acetic anhydride (55 µL, 5.09 mmol) at room temperature overnight. The excess of reagents were removed *in vacuo*, and the residue was dissolved with CH_2Cl_2 and washed with brine. The organic extracts were dried and evaporated to give a residue. Chromatography (10:90 MeOH-CH_2Cl_2) afforded **9** (14 mg, 42%) as an oil: ^{1}H NMR 1.45-2.70 (m, 9H), 1.89 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.91 (t, J = 3 Hz, 1H, H-7a), 3.10 (m, 1H, H-2$_\alpha$), 5.48 (dd, J = 8.5, 2.5 Hz, 1H, H-4$_{ax}$), 7.35 (t, J = 8 Hz, 1H), 7.48 (t, J = 8 Hz, 1H), 7.53 (d, J = 8 Hz, 1H), 7.68 (d, J = 8 Hz, 1H); ^{13}C NMR 17.8 (C-6), 21.0 (CH_3), 22.2 (C-7), 25.9 (C-5), 34.4 (C-3), 39.7 (NCH_3), 52.5 (C-3a), 54.1 (C-2), 69.4 (C-7a), 76.9 (C-4), 125.7 (C-3'), 127.4 (C-4'), 130.6 (C-6'), 131.2 (C-5'), 136.2 (C-1'), 152.2 (C-2'), 170.3 (OAc); HRMS Calcd for $C_{17}H_{22}N_2O_4$ 318.1570, found 318.1580.

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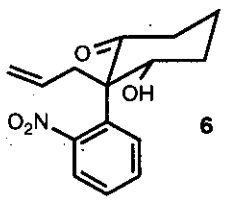

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