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^{1}H NMR Study of Conformational Differences in 3-*tert*-Butyldimethylsiloxy- and 9-Methyl-8-oxa-9-azabicyclo[3.2.2]non-6-en-3-ol Intermediates for Bridgehead Hydroxylated Tropane Alkaloid Derivatives

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The stereochemistry of bicyclic oxazepane-type intermediates for the synthesis of hydroxylated tropane alkaloids was determined by ^{1}H NMR spectroscopy. Thermolysis of the 3α-*tert*-butyldimethylsiloxy-8-methyl-8-azabicyclo[3.2.1]oct-6-ene axial *N*-oxide diastereomer (1) in butyronitrile afforded the Meisenheimer rearrangement product, (1*R, 3*S**, 5*S**)-3-(*tert*-butyldimethylsiloxy)-9-methyl-8-oxa-9-azabicyclo[3.2.2]non-6-ene (2). NMR techniques have shown that this product experiences a conformational bias favoring occupancy of the bulky 3-*tert*-butyldimethylsiloxy substituent in an *exo*-disposed equatorial position on a boat oxazepane ring. It was found the *tert*-butyldimethylsiloxycycloheptenylamino fragment in 2 retained the same relative stereochemistry as ascribed to this moiety in the starting material 1. Removal of the bulky *tert*-butyldimethylsilyl protecting group afforded 5, having a less sterically demanding 3-hydroxy substituent, and resulted in an equilibrium between the boat and chair oxazepane ring conformations. © 1997 by John Wiley & Sons, Ltd.**

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INTRODUCTION

Starting from scopolamine, it has recently been shown that thermolysis of the 3α-*tert*-butyldimethylsiloxy-8-methyl-8-azabicyclo[3.2.1]oct-6-ene axial *N*-oxide diastereomer **1** in butyronitrile affords a single Meisenheimer rearrangement product (**2**) (as a racemate), which was then elaborated in a series of reactions to afford a 3-hydroxy analogue (**3** ⇄ **3a**) of physoperuvine, a tropane alkaloid.[1]

The *tert*-butyldimethylsilyl-protected cyclohepta-3,5-dienyl-1-ol **4** was also isolated from the *N*-oxide thermolysis reaction in addition to **2**.[1] A separate experiment showed that **4** was produced from **2**, presumably as a result of a retro-Diels–Alder reaction.[1] Previously, Kibayashi and co-workers[2] and Malpass and co-workers[3] described the preparation of oxazabicyclic **2**-type ring systems by Diels–Alder addition reactions. The finding of only one diastereomer for **2** from the *N*-oxide thermolysis suggests that it derives directly from a Meisenheimer rearrangement with concomitant retention of the 3-siloxy relative stereochemistry. However, this supposition had to be proven since an important part of the physoperuvine-type product (**3** ⇄ **3a**) structure proof was to be based upon retention of the relative stereochemistry in **2** *vs.* that of the 3-*tert*-butyldimethylsiloxycyclohept-6-enylamino fragment in the starting material **1**. The NMR characterization of the stereochemistry of the rearrangement product **2**, and that of its corresponding free hydroxyl derivative **5** resulting from removal of the protecting group is presented in this paper.

RESULTS AND DISCUSSION

The ^{1}H and ^{13}C NMR ($CDCl_3$) spectral parameters for both **2** and **5** are listed in Table 1. Homonuclear spin–spin splitting networks were ascertained by homonuclear proton decoupling and by COSY-90 RELAY 2D NMR experiments. ^{13}C multiplicities were determined by a full set of DEPT experiments (135°, 90° and 45° pulse widths). ^{1}H–^{13}C connectivities were determined by short-range [^1J(CH)] heteronuclear correlation (XHCORR) 2D NMR experiments. The numbering diagram for these compounds is provided by

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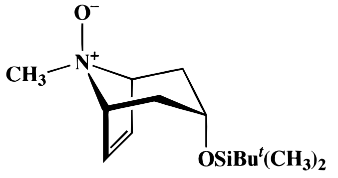

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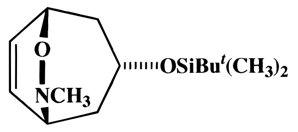

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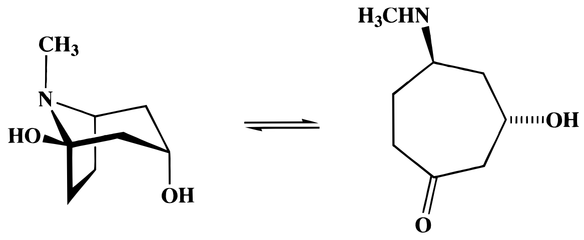

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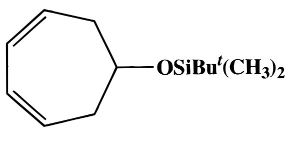
3a



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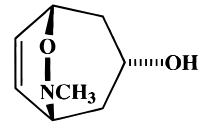

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structure **6**, where, similarly to the practice of x-ray crystallography, an extra digit in the descriptor differentiates each nucleus within a diastereotopic pair (e.g. H-21 and H-22 are both ligated to C-2, etc.).

^{1}H NMR details of compound 2

The H-1 nucleus appears as part of an apparent five-spin system since it affords a multiplet having 16 transitions in 10 lines in the ratio 1:2:1:1:3:3:1:1:2:1. The order of the transitions is 1, [2, 3], 4, 5, [6, 7, 9], [8, 10, 11], 12, 13, [14, 15], 16 due to six overlaps, four of which emanate from $J(1\text{–}21) \approx J(1\text{–}6)$ and two from $J(1\text{–}22) \approx [\,J(1\text{–}21) + J(1\text{–}7)]$. There are three vicinal neighbors, plus H-1 itself, making a total of four spins (i.e. eight transitions in a maximum of eight lines). Therefore, the extra set of eight transitions must be due to an additional spin (long-range allylic coupling).

H-21 is part of an apparent four-spin system. However, its H-22 diastereotopic partner appears as part of an apparent five-spin system since it affords a multiplet having 16 transitions in 12 lines in the ratio 1:1:1:2:1:2:2:1:2:1:1:1. The order of the transitions is 1, 2, 3, [4, 5], 6, [7, 9], [8, 10], 11, [12, 13], 14, 15, 16 due to four overlaps, two of which arise from $J(21\text{–}3) \approx [\,J(22\text{–}42) + J(22\text{–}3)]$ and two from $J(21\text{–}22) \approx [\,J(22\text{–}42) + 2J(22\text{–}3)]$. Again, since there are one geminal and two vicinal neighbors, plus H-22 itself, the extra set of eight transitions must then be due to an additional spin [long-range 'W'-type four-bond (^4J) coupling].

H-3 is part of an apparent five-spin system and appears as a multiplet having 16 transitions in nine lines in the ratio 1:2:2:1:4:1:2:2:1. The order of transitions is 1, [2, 3], [5, 9], *4*, [6, 7, 10, 11], *13*, [8, *12*], [14, 15], 16 due to seven overlaps, four of which emanate from $J(22\text{–}3) \approx J(3\text{–}42)$ and three from $J(21\text{–}3) \approx J(3\text{–}41)$. There are two inversions of order since $J(3\text{–}41) < [\,J(22\text{–}3) + J(3\text{–}42)]$.

Like H-21, H-41 is part of an apparent four-spin system. Its H-42 diastereotopic partner is part of an apparent five-spin system (due to long-range 'W'-type coupling) and affords a multiplet having 16 transitions in 13 lines (one more than found for H-22). These lines are in the ratio 1:1:1:2:1:1:2:1:1:2:1:1:1 in which the order of the transitions is 1, 2, 3, [4, 5], 6, 7, [8, 9], 10, 11 [12, 13], 14, 15, 16 due to three overlaps, two of which arise from $J(42\text{–}5) \approx [\,J(22\text{–}42) + J(3\text{–}42)]$ and one more since $J(41\text{–}42) \approx [\,J(22\text{–}42) + J(3\text{–}42) + J(42\text{–}5)]$.

Owing to long-range allylic coupling, the H-5 nucleus is also part of an apparent five-spin system and affords a 'triplet of triplets'-type of multiplet having 16 transitions in nine lines in the ratio 1:2:1:2:4:2:1:2:1. The order of the transitions is 1, [2, 3], 4, [5, 9] [6, 7, 10, 11], [8, 12], 13, [14, 15], 16 due to seven overlaps, four of which arise from $J(5\text{–}7) \approx J(41\text{–}5)$ and three from $J(5\text{–}6) \approx J(42\text{–}5)$.

Finally, the vinylic H-6 and H-7 nuclei are each part of an apparent four-spin system due to allylic-type long-range coupling. H-6 has only four broadened transitions

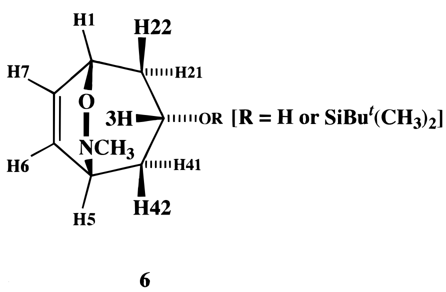

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Table 1. ^1H and ^{13}C spectral parameters and calculated proton–proton vicinal coupling constants for (1*R, 3*S**, 5*S**)-3α-(*tert*-butyldimethylsiloxy)-9-methyl-8-oxa-9-azabicyclo[3.2.2]non-6-ene (2) and (1*R**, 3*S**, 5*S**)-9-methyl-8-oxa-9-azabicyclo[3.2.2]non-6-en-3α-ol (5)**

δ_H (ppm)[a]	2	5	δ_C (ppm)[b]	2	5
H-1	4.44	4.48	C-1	68.77	69.46
H-21	1.53	1.77	C-2	40.98	41.49
H-22	2.32	2.38	C-3	68.80	67.61
H-3	4.51	4.34	C-4	39.78	39.86
H-41	1.60	1.90	C-5	57.56	58.12
H-42	2.38	2.46	C-6	129.55	130.06
H-5	3.48	3.53	C-7	132.50	132.83
H-6	6.25	6.36	NCH_3	46.65	46.22
H-7	6.46	6.56	$C(CH_3)_3$	17.87	—
NCH_3	2.62	2.59	$C(CH_3)_3$	25.73	—
$C(CH_3)_3$	0.86	—	$SiCH_3$	−4.78	—
$SiCH_3$	0.05_5	—	$SiCH_3$	−4.78	—
$SiCH_3$	0.06_1	—			

	Experimental J(HH) (Hz)[c]		Calculated J(HH) (Hz)[d]					
			Boat-**2**	Chair-**2**	9:1[e]	Boat-**5**	Chair-**5**	6:4[e]
1-21	0.9 (2)	2.2 (1)	1.2 [90]	4.1 [44]	1.5	1.1 [89]	4.1 [44]	2.3
1-22	7.3 (5)	5.7 (2)	8.1 [28]	2.2 [73]	7.5	8.1 [28]	2.2 [72]	5.7
1-6	1.0 (2)	0.5 (1)						
1-7	6.7 (2)	6.6 (2)						
21-3	9.4 (1)	6.6 (1)	10.6 [167]	1.8 [78]	9.7	10.4 [165]	1.8 [78]	7.0
22-3	6.0 (4)	5.8 (1)	5.6 [50]	4.8 [39]	5.5	6.0 [48]	4.8 [39]	5.5
21-22	−13.3 (5)	−13.9 (1)						
21-41	Not observed	1.0 (1)						
22-42	1.1 (2)	Not observed						
3-41	9.4 (1)	6.8 (1)	10.6 [167]	1.6 [81]	9.7	10.4 [165]	1.5 [82]	6.8
3-42	6.1 (2)	5.6 (3)	5.5 [51]	5.5 [35]	5.5	5.8 [49]	5.6 [34]	5.7
41-42	−13.1 (2)	−13.9 (1)						
41-5	1.5 (1)	3.7 (1)	0.9 [83]	4.5 [41]	1.3	0.9 [83]	4.1 [44]	2.2
42-5	7.1 (1)	5.2 (2)	7.2 [34]	2.0 [75]	6.7	7.2 [34]	2.2 [73]	5.0
5-6	7.1 (1)	7.0 (1)						
5-7	1.4 (1)	1.4 (1)						
6-7	9.2 (1)	9.2 (1)						

[a] Ppm downfield from tetramethylsilane, 300.1 MHz (for **2**), 399.9 MHz (for **5**), $CDCl_3$.

[b] Ppm downfield from tetramethylsilane, 75.5 MHz (for **2** and **5**), $CDCl_3$.

[c] Estimated standard deviations for the last digit given in parentheses.

[d] Calculated according to Refs 5 and 6 using dihedral angles from the appropriate boat or chair conformation AM1 model; dihedral angles (°) are given in square brackets.

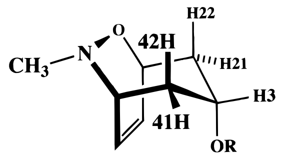
[e] Weighted average calculated vicinal coupling constants for the boat and chair conformations (90:10 ratio for **2** and 60:40 ratio for **5**).

(*ca.* 1.9 Hz width at half-height), while H-7 has eight transitions in eight lines since $J(6–7) > [J(5–7) + J(1–7)]$.

In a similar manner, one can account for all the observed intensities and number of lines of the multiplets in **5** based on the measured coupling constants listed in Table 1.

Stereochemistry

There are two seven-membered rings sharing common atoms in the Meisenheimer rearrangement product **2**. Four models (**7**–**10**) differing in oxazepane-ring conformation and C-3 configuration may be considered for this compound. Two (1*R**, 3*S**, 5*S**)-models (**7** and **8**) retain similar stereochemistry to **1**, whereas the two (1*R**, 3*R**, 5*S**)-models (**9** and **10**) depict C-3 with an inversion of configuration. The finding of 9.4 and 6.0 Hz unequal magnitude vicinal coupling constants involving the protons in the C-2—C-3 and C-3—C-4 bonds is not consistent with the four synclinal-type (*ca.* 60°) H—C—C—H dihedral angle arrangements expected for an *endo*-disposed axially-oriented *tert*-butyldimethylsiloxy group as illustrated in **7** or **10**. The large steric bulk expected for the *tert*-butyldimethylsiloxy moiety would also argue against such an *endo* disposition. The equatorial methylene protons, assigned as H-22, H-42 in model **8** and H-21, H-41 in model **9**, have synclinal-type (*ca.* 60°) relationships to H-3, whereas their geminal diastereotopic axial neighbors show antiperiplanar-type (*ca.* 180°) arrangements involving H-3. The 9.4 and 6.0 Hz magnitudes of the vicinal coupling constants in the C-2—C-3 and C-3—C-4 bonds represent reasonable values expected for the model **8** and **9** antiperiplanar-type and synclinal-type dihedral angles in these bonds. The assignment of equatorial descriptors to the H-22 and H-42 methylene protons is also in accord with the observation of a 1.1(2) Hz ^4J long-range coupling between these two nuclei.



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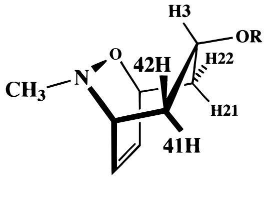

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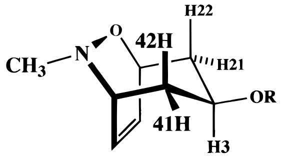

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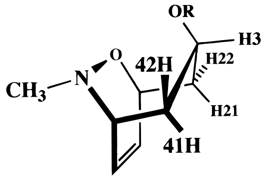

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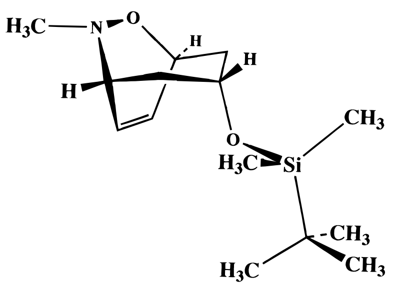
Such long-range coupling is usually associated with a 'W-type' diequatorial arrangement.

Nuclear Overhauser effect experiments (NOEDIFF) can be used to distinguish model **8** from **9**, since the vinylic and equatorial methylene protons are on opposite sides of the cycloheptenyl ring in **8**, whereas they are on the same side in **9**. The equatorial methylene protons are close to the vinylic protons in the chair conformation oxazepane rings (models **7** and **9**), whereas it is the axial counterparts that are close in the boat conformation oxazepane rings (models **8** and **10**). Upon {δ 6.25, H-6}, a 1.1% intensity enhancement was observed for the axial H-41 signal at δ 1.60, and a small 0.3% intensity increment was noted for the $\mathrm{NC}H_3$ protons at δ 2.62, while {δ 1.60, H-41} gave a 0.7% intensity increase for δ 6.25 (H-6). Similarly, upon {δ 6.46, H-7}, a 1.0% intensity enhancement was observed for the axial H-21 signal at δ 1.54. No intensity increment was measured for any of the equatorially disposed protons H-22, H-42 upon irradiation of either vinylic H. Irradiation of the $\mathrm{NC}H_3$ protons {δ 2.62} afforded 7.1, 1.4 and 0.7% intensity enhancements for the δ 3.48 (H-5), 6.25 (H-6) and 6.46 (H-7) signals, respectively, while no NOE was observed for either of the equatorial protons H-22, 42. Thus, the NOE experiments are in accord with model **8** in which the axial protons H-21, 41 and the *N*-methyl protons are close to the vinylic protons while the bulky $\mathrm{OSiBu}^t(\mathrm{CH_3})_2$ moiety is equatorially disposed on the boat conformation oxazepane ring.

Semi-empirical molecular models (AM1)[4] **11** and **12** were calculated for both **7** and **8** model types for product **2** [synperiplanar H-3—C-3—O—Si and antiperiplanar C-3—O—Si—*C*(Bu^t) torsion angles]. The heat of formation of the boat conformation **12** (model **8** type) was calculated to be 3.6 kcal mol^{-1} lower in energy compared with chair conformation **11** (model **7** type). Inspection of the relevant H—C—C—H dihedral angles in models **7** and **8** (listed in Table 1) shows that the bulky 3-*tert*-butyldimethylsiloxy substituent has resulted in a conformational bias by its occupation of an *exo*-disposed equatorial orientation on a boat oxazepane ring. Either a single conformational model, **8**, or a vast preponderance of this contributor appears to account for the magnitudes of all the corresponding vicinal coupling constants found for **2**. NMR spectroscopic techniques can therefore effectively eliminate models **7**, **9** and **10** from consideration, thereby leaving model **8** (depicted by **12**) as the preferred conformation for the Meisenheimer rearrangement product **2**. As a result of the structure proof for **2**, it was found that the 3-*tert*-butyldimethylsiloxycyclohept-6-enylamino fragment in the single Meisenheimer rearrangement-type diastereomer (**2**) that was isolated retained the same relative stereochemistry as in starting material (1*R**, 3*S**, 5*S**)-**1**, consistent with the diradical mechanism accepted for this rearrangement which would not involve any interaction with position **3**.

While the *tert*-butyldimethylsilyl protecting group is ordinarily removed in the last step of a multistep route to yield **3**, the finding of an equatorially oriented $\mathrm{OSiBu}^t(\mathrm{CH_3})_2$ moiety on a boat-conformation oxazepane ring suggested that removal of the bulky protect-



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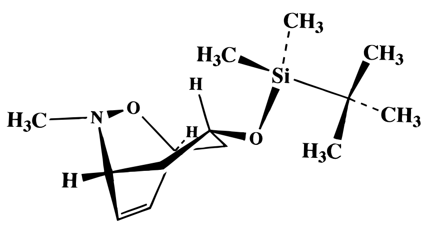

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ing group in **2** could result in a boat-to-chair conformational change due to an axially disposed hydroxy function in **5**. Inspection of Table 1 shows that each of the two diastereotopic protons on either C-2 or C-4 in **5** have a similar magnitude vicinal coupling constants with H-3, i.e. $J(21–3)$ 6.6(1) and $J(22–3)$ 5.8(4) Hz for the C-2—C-3 bond and $J(3–41)$ 6.8(1) and $J(3–42)$ 5.6(3) Hz for the C-3—C-4 bond. Since the configuration at C-3 remains invariant after removal of the *tert*-butyldimethylsilyl protecting group, only two models (**7** and **8**) need be considered for the structure of **5**. While the 6.6(1) and 6.8(1) Hz values are too small to be consistent with antiperiplanar-type H—C—C—H dihedral angles in model **8** [as opposed to the 9.4(1) Hz values found for **2**], these magnitudes are *too large* for those expected to arise from synclinal-type H—C—C—H angles in model **7** having an axially oriented hydroxy group. This suggests that a rapid equilibrium between the two conformations depicted in models **7** and **8** should be considered, since the observed vicinal coupling constants appear to represent weighted time-averaged values at the fast exchange limit for interconversion.

As before, semi-empirical molecular models (AM1) were calculated for both **7** and **8** model types of compound **5**. While the calculated energy difference between the boat and chair oxazepane ring conformations was smaller for models of **5** than for **2**, the boat model (**8**) was still lower in energy by 2.7 kcal mol^{-1}. Calculated H—C—C—H dihedral angles in **7** and **8** model types for compounds **2** and **5** were used as the input for estimating the corresponding vicinal coupling constants according to Altona's[5,6] generalized Karplus[7] relationship. While the calculated coupling constants are an approximation, the relationship does take orientation and electronegativity effects into consideration.[5] The estimated J(HH) values, and their corresponding dihedral angles given in square brackets, are also listed in Table 1. Inspection of these calculated values shows that no *single* conformational model can account for the vicinal coupling constants experimentally measured for **5**. A reasonable fit of eight calculated ^3J(HH) values with their experimentally determined counterparts was obtained using a 60:40 weighted average for the boat:chair conformations of **5**, while a more biased amount of the boat conformation (>90%) was estimated for **2** (see Table 1).

While time-averaged values are now expected for *all* the NMR spectral parameters (chemical shifts, coupling constants and NOE intensity enhancements) of **5**, there is other clear evidence (in addition to the vicinal coupling constants) for a contribution from the chair conformation oxazepane ring model **7**. The *trans*-to-nitrogen methylene protons at C-2 and C-4 absorb at δ 1.53 and 1.60 (H-21 and H-41, respectively) and are diaxially disposed in **2**, whereas their geminal diequatorial *cis*-to-nitrogen diastereotopic counterparts in this compound are found at δ 2.32 and 2.38 (H-22 and H-42, respectively). These protons are found at similar chemical shift values in **5**: δ 1.77 and 1.90 (H-21 and H-41, respectively) and δ 2.38 and 2.46 (H-22 and H-42, respectively). NOE experiments have shown that the same H-21 and H-41 descriptors can still be assigned to *trans*-to-nitrogen methylene protons at C-2 and C-4 in **5**. A small 0.2% NOE intensity enhancement was found for the H-21 resonance at δ 1.77 upon $\{\delta$ 6.56, H-7$\}$, and a similar 0.2% increased intensity was found for the H-41 resonance at δ 1.90 upon $\{\delta$ 6.36, H-6$\}$, whereas no intensity increment was measured for either of the diastereotopic H-22, 42 protons upon irradiation of the vinylic H. However, it is these *trans*-to-nitrogen H-21 and H-41 nuclei that show a 1.0(1) Hz ^4J long-range coupling usually associated with a 'W-type' diequatorial arrangement between the two protons (as opposed to **2** where it arises from the *cis*-to-nitrogen H-22, 42 pair). A diequatorial arrangement for the H-21, 41 protons is compatible with a model **7** chair conformation for the oxazepane ring, but not for boat model **8**. Thus, after removal of the bulky *tert*-butyldimethylsilyl protecting moiety, the resulting smaller and less sterically demanding hydroxy functionality appears to enable the oxazepane ring to also bend into a chair conformation (although the boat conformation still remains an important contributor as judged by the magnitudes of the averaged vicinal coupling constants). As in the case of **2**, the *N*-methyl group in **5** is close to the etheno bridge: $\{\delta$ 2.59, N$CH_3\}$ gives a 0.6 and 0.2% intensity increase to the respective vinylic H-6 and H-7 protons (no NOE was found for the *cis*-to-nitrogen H-22, 42 protons).

In conclusion, analysis of multi-line/multi-intensity NMR multiplets has been presented and then used to study the stereochemistry of bicyclic oxazepane-type intermediates for the synthesis of hydroxylated tropane alkaloids. Homonuclear vicinal constants and nuclear Overhauser effects have shown that the 3-(*tert*-butyldimethylsiloxy)-9-methyl-8-oxa-9-azabicyclo[3.2.2]non-6-ene product (**2**) experiences a conformational bias favoring occupancy of the bulky 3-siloxy substituent in an *exo*-disposed equatorial position on a boat oxazepane ring. Removal of the bulky *tert*-butyldimethylsilyl protecting group affords **5** with a less sterically demanding 3-hydroxy substituent. The coupling constants and nuclear Overhauser effects measured for **5** are consistent with an equilibrium between the boat and chair oxazepane ring conformations.

EXPERIMENTAL

Compounds

(1*R, 3*S**, 5*S**)-3α-*tert*-Butyldimethylsiloxy-9-methyl-8-oxa-9-azabicyclo[3.2.2]non-6-ene (2).** A solution of 3α-*tert*-butyldimethylsiloxy-8-methyl-8-azabicyclo[3.2.1]oct-6-ene *N*-oxide (**1**) (1.56 g, 5.8 mmol), potassium carbonate (1 g) and butyronitrile (25 ml) was refluxed for 2 h. The solution was filtered and the solvent removed from the filtrate under reduced pressure. The Meisenheimer rearrangement product (1*R**, 3*S**, 5*S**)-3α-*tert*-butyldimethylsiloxy-9-methyl-8-oxa-9-azabicyclo[3.2.2]non-6-ene (**2**)[1] (0.83 g, 3.1 mmol, 53%) was isolated as an oil by flash column chromatography on silica gel with 5% methanol–dichloromethane as eluent. MS (EI), *m/z* 269 (M$^+$, 0.8%; calculated for $C_{14}H_{27}NO_2Si$, 269.1811; found, 269.1807), 226 (13), 144 (13), 101 (20) and 75 (100); IR (neat) 2952, 2928, 2856, 1647, 1462, 1257, 1085, 883, 836 and 775 cm^{-1}.

(1*R, 3*S**, 5*S**)-9-Methyl-8-oxa-9-azabicyclo[3.2.2]non-6-en-3α-ol (5).** A solution of **2** (0.15 g, 0.56 mmol) in 3% aqueous HCl (15 ml) was stirred overnight at room temperature. The solution was then basified with concentrated aqueous NH_3 and the solvent was removed under reduced pressure to leave a white solid. This solid was extracted with acetone to yield, after evaporation of the acetone, (1*R**, 3*S**, 5*S**)-9-methyl-8-oxa-9-azabicyclo[3.2.2]non-6-en-3α-ol (**5**)[1] as an oil (0.090 g, 0.53 mmol, 96%). MS (EI), *m/z* 155 (M^+, 35%; calculated for $C_8H_{13}NO_2$, 155.0946; found, 155.0942), 133 (34), 110 (42), 82 (100) and 44 (97).

Spectra

^1H NMR (300.1 MHz for **2** and 399.9 MHz for **5**) and ^{13}C NMR (75.5 MHz for **2** and **5**) spectroscopy was performed on Varian Unity 300 and 400 spectrometers. $CDCl_3$ was used for the lock signal and tetramethylsilane was used as the internal spectral reference. Standard Varian pulse library programs were used for RELAY COSY, DEPT, XHCORR and NOEDIFF experiments. High-resolution mass spectra were obtained using a Fisons/VG Autospec-OA-TOF mass spectrometer. FT-IR spectra were recorded as films (neat) with a Digilab FTS-7 spectrometer and an NaCl disk. AM1 semi-empirical calculations were performed on a Macintosh Quadra 950 computer equipped with an Apple PowerMacintosh upgrade card using the CS-CHEM3D Pro 3.5/CS-MOPAC Pro 3.5 program combination.[4] Iconic two-dimensional projections (**11** and **12**) of the AM1 three-dimensional model **7** and model **8** types for **2**, respectively, were produced by the CS-CHEM3D Pro 3.5/CS-CHEMDRAW Pro 3.5.1 program combination.[8]

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