Stereospecific Synthesis of *cis*-2-Alkoxy-3-aminooxolanes

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cis-2-Alkoxy-3-aminooxolanes **4** were synthesized in a remarkably stereospecific manner by alcoholysis of α-chloro-γ-((trimethylsilyl)oxy)ketimines **2**, obtained by alkylation of α-chloroketimines **1** with 2-bromo-1-((trimethylsilyl)oxy)ethane. The stereospecificity of the cyclization was lost when the alcoholysis was performed in the presence of base. However, complete transformation of the mixtures of *cis*- and *trans*-2-alkoxy-3-aminooxolanes into the more stable *cis*-compounds was achieved with hydrogen chloride in methanol. A mechanistic rationale for these stereochemical aspects is presented.

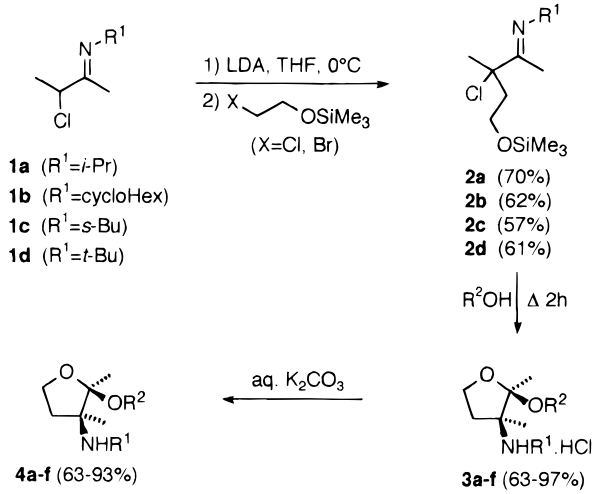
Introduction

α-Chloroimines[1] and ω-functionalized imines[2] have been shown to be valuable building blocks for the synthesis of heterocyclic compounds. The combination of both functionalities at the α- and ω-position in one molecule offers the potential to provide access to a variety of functionalized heterocyclic compounds, *e.g.* cyclic ethers. In the present paper, the synthesis of 2-alkoxy-3-(*N*-alkylamino)tetrahydrofurans **4** from α-chloro-γ-((trimethylsilyl)oxy)ketimines **2** is investigated. Until now only a few syntheses of these 2-alkoxy-3-aminooxolanes **4** were reported in the literature.[3,4] However, these compounds have a potential interest from the viewpoint that they are related to amino sugars, which display important biological activities.[5]

Results and Discussion

α-Chloro-γ-((trimethylsilyl)oxy)ketimines **2** were synthesized by regiospecific alkylation[6] of α-chloroketimines **1** with 2-bromo-1-((trimethylsilyl)oxy)ethane *via* the intermediacy of 3-chloro-1-azaallylic anions, generated with lithium diisopropylamide in tetrahydrofuran (Scheme 1). 2-Chloro-1-((trimethylsilyl)oxy)ethane could be used as well but resulted in somewhat more unreacted starting materials. These α,γ-difunctionalized ketimines **2** were purified by vacuum distillation (57−70% yield) and have a reasonable shelf life, provided they are well protected from moisture under nitrogen in the refrigerator.

Scheme 1



Reaction of α-chloro-γ-((trimethylsilyl)oxy)ketimines **2** with methanol, ethanol, or 1-propanol (10% solution w/v) under reflux for 2 h resulted in a very clean reaction leading to virtually pure hydrochlorides of *cis*-2-alkoxy-3-aminooxolanes **3**, which were simply isolated by evaporation of the solvent under vacuum (yield 84−97% except 63% for compound **3f** (R^1 = *s*-Bu, R^2 = *n*-Pr)). The free bases **4** were obtained by treatment of the solid hydrochlorides **3**, dissolved in dichloromethane, with aqueous potassium carbonate and extraction with dichloromethane (Scheme 1, Table 1). The alcoholysis of the difunctionalized ketimines **2** afforded no trace of the stereoisomeric *trans* compounds **14** as verified by extensive spectroscopic and chromatographic analyses.

The relative position of the substituents at the 2- and 3-position of the tetrahydrofuran rings **4** was determined by comparison of the ^{13}C-NMR spectral data of the *cis* derivative **4a** and *trans* derivative **14a** (*vide infra*). In related furanosides a 5−6 ppm upfield shift for *C*-1 signals (^{13}C NMR) arising from *cis*-1,2-disubstituted compounds in comparison with *trans*-1,2-disubstituted compounds has been reported.[4,7] Thus, the *cis* configuration was assigned to the tetrahydrofuran derivative **4a**, having a signal for *C*-2 at δ 106.86, which is 2.6 ppm upfield as compared to the *C*-2 signal of the corresponding

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(2) Stevens, C.; De Kimpe, N. *J. Org. Chem.* **1993**, *58*, 132−134.
(3) (a) Kralinina, L. N.; Kruglikova, R. I.; Bogomolova, V. I. *Khim. Geterotsikl. Soedin.* **1970**, 299−301; *Chem. Abstr.* **1970**, *73*, 55896j. (b) For the synthesis of some more substituted 2-alkoxy-3-aminooxalanes see for example: de Guchteneere, E.; Fattori, D.; Vogel, P. *Tetrahedron* **1992**, *48*, 10603−10620. Guidicelli, M.-B.; Picq, D.; Anker, D. *Tetrahedron* **1992**, *48*, 6033−6042. Shiozaki, M.; Ishida, N.; Sato, S. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3950−3958.
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(5) Hauser, F.; Ellenberger, S. *Chem. Rev.* **1986**, *86*, 35−67.
(6) De Kimpe, N.; Sulmon, P.; Schamp, N. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 881−882.

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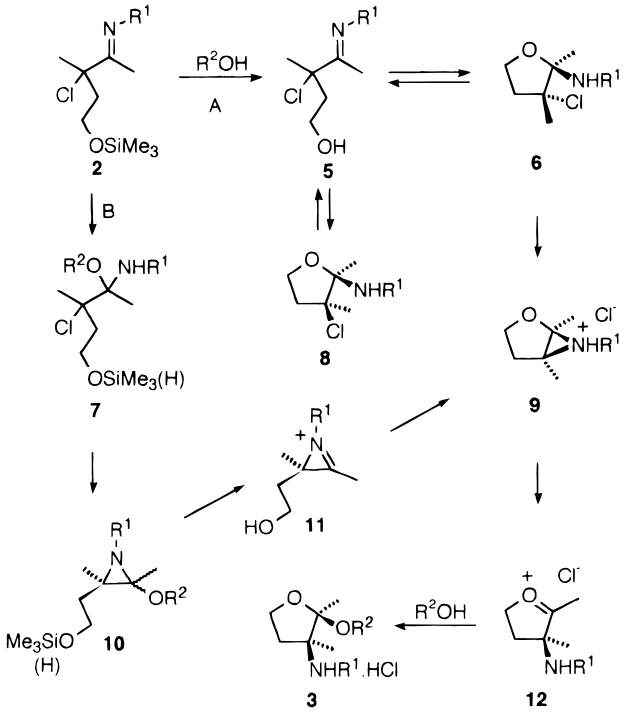
Table 1. Synthesis of *cis*-2-Alkoxy-3-aminooxolane Hydrochlorides 3 and the Corresponding Free Bases 4

entry	substrate **2**	R^2,[a] (alcohol)	reaction product **3** (yield, %)[b]	oxolane **4**[c] (yield, %)[d]
1	**2a** (R^1 = *i*-Pr)	Me	**3a** (89)	**4a** (91)
2	**2a** (R^1 = *i*-Pr)	Et	**3b** (84)	**4b** (87)
3	**2b** (R^1 = cyclohex)	Me	**3c** (93)	**4c** (92)
4	**2c** (R^1 = *s*-Bu)	Me	**3d** (87)	**4d** (88)
5	**2c** (R^1 = *s*-Bu)	Et	**3e** (97)	**4e** (85)
6	**2c** (R^1 = *s*-Bu)	n-Pr	**3f** (63)	**4f** (93)

[a] Reaction of imines **2** with the alcohol R^2OH (10% w/v) under reflux for 2 h. [b] Crude yields after evaporation of the alcohol (purity > 98%, *c*/*t* > 98%; ^{1}H- and ^{13}C-NMR). [c] Free bases **4** were obtained by treatment of the hydrochlorides **3** with aqueous potassium carbonate at room temperature. [d] Crude yields (purity ≥ 98%; *c*/*t* > 98%; capillary GC, ^{1}H- and ^{13}C-NMR).

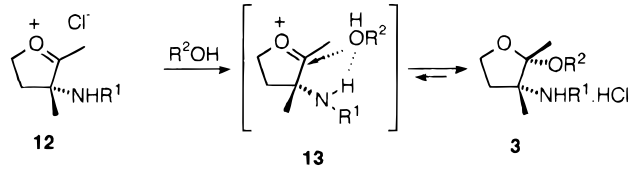
Scheme 2



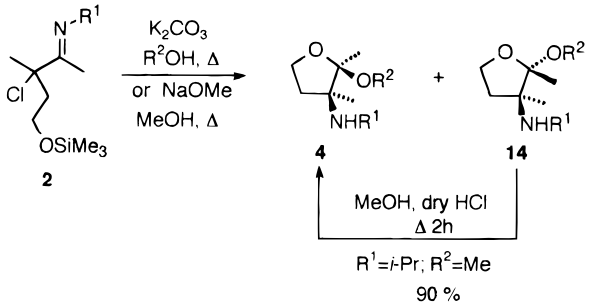
trans isomer **14a** (δ 109.42) in ^{13}C NMR spectroscopy. The final unambiguous proof of the *cis*-stereochemistry of the functionalized oxolanes **3** was obtained from X-ray crystallographic analysis[8] of the hydrochloride of 3-(*N*-isopropylamino)-2-methoxy-2,3-dimethyloxolane **3a**, obtained from the reaction of imine **2a** (R^1 = *i*-Pr) with methanol under reflux for 2 h. Because of the small difference in chemical shifts of the methyl groups at *C*-2 and *C*-3, attempts to determine the stereochemistry by DIFNOE were unsuccessful.

From a mechanistic point of view the course of the reaction is explained by oxygen desilylation (route A) and addition of the alcohol function across the imino bond to give either the *cis*-oxolane **8** or the *trans*-oxolane **6** (Scheme 2). This reversible reaction leads to the bicyclic aziridine intermediate **9** having both methyls in a *cis* disposition. Alternatively (route B), the α-chloroketimine **2** can undergo addition of the alcohol with subsequent ring closure to α-alkoxyaziridine intermediate **10**,[9] which can generate the transient 6-aza-2-oxabicyclo[3.1.0]hexane derivative **9** in a stereospecific manner. Both routes A and B are viable routes and lead to the same stereospecific result, i.e. intermediate **9**. Under the given solvolytic conditions, this hemiaminal intermediate **9** opens up to the oxonium species **12**, which suffers a stereospecific attack of the alcohol to afford *cis*-**3**. This process might be explained by hydrogen bonding between the amino group of the oxonium species **12** and the approaching alcohol, directing the attack on the same side as the amino group (Scheme 3).[4] Ammonium groups also have shown to be very efficient in directing the epoxidation of alkenylamines with *m*-CPBA and dimethyldioxirane on the *syn*-diastereoface by H-bonding interaction between the ammonium group and the O-transfer reagent.[10] The *cis*-isomer **3** is probably the thermodynamically favored isomer because, once formed, it might be stabilized by internal hydrogen bonding. Therefore, alternatively, formation of the *cis*-isomer **3** can be explained as resulting from the equilibration of the initially formed *cis*- and *trans*-isomers **3** and **14**·HCl *via* intermediate **12** (*vide infra*).

Scheme 3



Scheme 4



When α-chloro-γ-((trimethylsilyl)oxy)ketimines **2** were reacted with methanol or ethanol in the presence of 3 mol equiv of potassium carbonate, the reaction led to a mixture of *cis*- and *trans*-2-alkoxy-3-aminooxolanes **4** and **14** in varying ratios (from 5:1 to 2:3, or vice versa) (Scheme 4). With sodium methoxide in methanol, α-chloroketimine **2a** (R^1 = *i*-Pr) gave rise to *trans*-2,3-dimethyl-3-(*N*-isopropylamino)-2-methoxyoxolane **14a** (R^1 = *i*-Pr; R^2 = Me) mainly (**14a**:**4a** > 7:1) in 81% yield (Table 2). In the presence of base, the stereospecificity of the cyclization process is lost, resulting in varying mixtures of *cis*- and *trans*-oxolanes **4** and **14**.

The predominant formation of the *trans*-isomer **14a** when ketimine **2a** was subjected to the action of the stronger base sodium methoxide can be rationalized by assuming a kinetically favored attack of methoxide from

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(8) An ORTEP diagram is included in the Supporting Information for this article. The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

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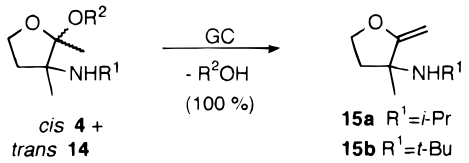
(10) Asensio, G.; Mello, R.; Boix-Bernardini, C.; González-Núñez, M. E.; Castellano, G. *J. Org. Chem.* **1995**, *60*, 3692−3699.

Table 2. Synthesis of *cis*- and *trans*-2-Alkoxy-3-(*N*-alkylamino)-2,3-dimethyltetrahydrofurans 4 and 14 by Reaction of α-Chloro-γ-((trimethylsilyl)oxy)ketimines 2 with Alcohol in the Presence of Base

entry	R^1	base, alcohol (R^2OH)	reaction time (h)[a]	ratio of **4**/**14**	yield[b] (%)	bp (°C)/mmHg
1	*i*-Pr	K_2CO_3, MeOH	5	**4a**/**14a**: 3/5	70	25−27/0.2
2	*i*-Pr	NaOMe, MeOH	2	**4a**/**14a**: 1/7	100[c]	−
3	*i*-Pr	K_2CO_3, EtOH	4.5	**4b**/**14b**: 1/1	85[c]	−
4	cyclohex	K_2CO_3, MeOH	2.5	**4c**/**14c**: 5/1	53	50−53/0.005
5	cyclohex	K_2CO_3, EtOH	2.5	**4g**/**14g**: 2/3	34	61−69/0.02
6	*t*-Bu	K_2CO_3, MeOH	2.5	**4h**/**14h**: 3/2	59	38−40/0.1
7	*t*-Bu	K_2CO_3, EtOH	2.5	**4i**/**14i**: 5/1	90	40−42/0.05

[a] Reflux time. [b] After distillation. [c] Crude yield (purity > 90%).

Scheme 5



the less hindered side of the oxonium intermediate **12**, opposite to the *N*-alkylamino substituent at the 3-position.

To support our assumption that the *cis*-isomer **4a** is the thermodynamically most stable isomer, the mixture of *cis*- and *trans*-2,3-substituted oxolanes (**4a**/**14a**: 12/88) was treated with methanol, saturated with dry HCl, and heated under reflux. Indeed, thermodynamic equilibration of the mixture via the oxonium species **12**, resulting in a complete and very clean isomerization of *trans* **14a** to *cis* **4a**, was observed after 2 h.

During gas chromatographic treatment of the *cis*/*trans* mixture of 3-(*N*-alkylamino)-2-methoxy-2,3-dimethyloxolanes **4** and **14** (R^1 = *i*-Pr; R^2 = Me), both isomers were transformed into 3-(*N*-alkylamino)-3-methyl-2-methyleneoxolanes **15** (R^1 = *i*-Pr and *t*-Bu) in quantitative yield (Scheme 5).

In conclusion, a preparatively appealing method for the synthesis of *cis*-2-alkoxy-3-aminooxolanes, which may be of biological interest, was developed. These stable bifunctionalized oxygen heterocycles were accessible from α-chloro-γ-((trimethylsilyl)oxy)ketimines in high yields using facile experimental procedures amenable to large scale production.

Experimental Section

General. Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 270, 60 MHz and 68, 20 MHz, respectively, with Me_4Si as internal standard using $CDCl_3$ as solvent. The type of carbon and hydrogen atom was determined via DEPT, $^{13}C-^1H$- and $^1H-^1H$-COSY techniques. Mass spectra were performed at 70 eV. Preparative gas chromatographic analysis was performed using 8% SE-30 on Chromosorb W 60−80, 3 m (H_2 as carrier gas). Ether was dried and distilled from sodium wire, while tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl.

Synthesis of *N*-[3-Chloro-3-methyl-5-((trimethylsilyl)oxy)-2-pentylidene]alkylamines (2a−d).[6] A solution of LDA was prepared by addition of 2.5 M *n*-butyllithium (24 mL, 60 mmol) in hexane to an ice-cooled solution of diisopropylamine (6.56 g, 65 mmol) in dry THF (60 mL) under a nitrogen atmosphere. This solution was treated by syringe with a solution of α-chloroketimine **1**[11] (50 mmol) in THF (50 mL). After 1 h at 0 °C, 1-bromo-2-((trimethylsilyl)oxy)ethane (55 mol) in 30 mL of THF was added, and the reaction mixture was stirred for 20 h during which the mixture was allowed to reach room temperature. Then, the reaction mixture was poured into 0.5 N sodium hydroxide (200 mL) and extracted with diethyl ether (3 × 100 mL), and the combined extracts were dried (K_2CO_3). After filtration and removal of the solvent *in vacuo*, the crude α-chloro-γ-((trimethylsilyl)oxy)ketimines **2a**−**d** were distilled *in vacuo*.

***N*-[3-Chloro-3-methyl-5-((trimethylsilyl)oxy)-2-pentylidene]isopropylamine (2a):** bp 60−62 °C/0.05 mmHg; ^1H-NMR (60 MHz, CCl_4) δ 0.10 (9H, s, $Si(CH_3)_3$); 1.10 (6H, d, *J* = 6 Hz, $(CH_3)_2CH$); 1.70 (3H, s, CH_3CCl); 1.99 (3H, s, $CH_3C{=}N$); 2−2.4 (2H, m, CH_2CCl); 3.7 (1H, m, $CH(CH_3)_2$; 3.76 (2H, t, *J* = 7 Hz, CH_2O); ^{13}C-NMR (20 MHz) δ −0.5 ($Si(CH_3)_3$); 12.9 ($CH_3C{=}N$); 23.2 ($(CH_3)_2CH$); 28.4 (CH_3CCl); 44.5 (CH_2CH_2O); 50.7 ($CH(CH_3)_2$); 59.3 (CH_2O); 74.9 (CCl); 164.5 (C=N); IR (NaCl) 1651 cm^{-1} (C=N); MS (70 eV) *m*/*z* (%) no M^+; 248/50 ($M^+ - CH_3$; 7); 228 ($M^+ - Cl$; 5); 147/49(92); 132(17); 112(23); 96(20); 84(100); 73(21). Anal. Calcd for $C_{12}H_{26}ClNOSi$: C, 54.69; H, 9.94; N, 5.31. Found: C, 54.52; H, 10.06; N, 5.42.

***N*-[3-Chloro-3-methyl-5-((trimethylsilyl)oxy)-2-pentylidene]cyclohexylamine (2b):** bp 76−80 °C/0.002 mmHg; ^1H-NMR (270 MHz) δ 0.10 (9H, s, $Si(CH_3)_3$); 1.27−1.80 (10H, m, $(CH_2)_5$); 1.67 (3H, s, CH_3CCl); 1.96 (3H, s, $CH_3C{=}N$); 2.16−2.38 (2H, m, CH_2CH_2O); 3.23−3.33 (1H, m, CH); 3.59−3.79 (2H, m, CH_2O); ^{13}C-NMR (67.9 MHz) δ −0.5 ($Si(CH_3)_3$); 13.0 ($CH_3C{=}N$); 24.4, 25.7, and 33.0 ($(CH_2)_5$); 28.4 (CH_3CCl); 44.5 (CH_2CH_2O); 59.0 (CH); 59.3 (CH_2O); 75.1 (CCl); 164.7 (C=N). IR (NaCl) 1649 cm^{-1} (C=N). MS (70 eV) *m*/*z* (%) no M^+; 288/90 ($M^+ - CH_3$; 5); 268(4); 188/90(11); 187/89(59); 124(29); 106(20); 83(100); 55(35). Anal. Calcd for $C_{15}H_{30}ClNOSi$: C, 59.27; H, 12.44; N, 5.76. Found: C, 59.43; H, 12.30; N, 5.82.

***N*-[3-Chloro-3-methyl-5-((trimethylsilyl)oxy)-2-pentylidene]-*sec*-butylamine (2c):** bp 58−60 °C/0.005 mmHg; ^1H-NMR (270 MHz) δ 0.11 (total 9H, s, $Si(CH_3)_3$); 0.79 en 0.80 (3H, 2 × t, *J* = 7.4 Hz, $CHCH_2CH_3$); 1.02 and 1.03 (3H, 2 × d, *J* = 6.3 Hz, $CHCH_3$); 1.48 (2H, ∼pentuplet, *J* ∼ 7 Hz, $CHCH_2CH_3$); 1.68 and 1.69 (3H, 2 × s, CH_3CCl); 1.96 (3H, s, $CH_3C{=}N$); 2.22 (1H, ABdd, *J* = 13.7, 8.6 Hz, $HCHCH_2O$); 2.35 (1H, ABdd, *J* = 13.7, 8.6, 5.4 Hz, $HCHCH_2O$); 3.36 (1H, sextet, *J* = 6.3 Hz, $CHCH_3$); 3.61−3.81 (2H, m, CH_2O); ^{13}C-NMR (67.9 MHz) δ −0.5 ($Si(CH_3)_3$); 10.9 and 11.0 ($CHCH_2CH_3$); 13.2 and 13.2 ($CH_3C{=}N$); 20.7 and 20.7 ($CHCH_3$); 28.5 and 28.6 (CH_3CCl); 30.8 and 30.9 ($CHCH_2CH_3$); 44.5 and 44.5 (CH_2CH_2O); 56.7 and 56.8 ($CHCH_3$); 59.3 and 59.4 (CH_2O); 75.0 and 75.0 (CCl); 165.1 and 165.1 (C=N); IR (NaCl) 1656 cm^{-1} (C=N). MS (70 eV) *m*/*z* (%): no M^+; 262/4 ($M^+ - CH_3$; 4); 161/3(45); 132/4(21); 98(39); 73(21); 57(21); 42(100). Anal. Calcd for $C_{13}H_{28}ClNOSi$: C, 56.18; H, 10.16; N, 5.04. Found: C, 56.09; H, 10.11; N, 5.12.

***N*-[3-Chloro-3-methyl-5-((trimethylsilyl)oxy)-2-pentylidene]-*tert*-butylamine (2d):** bp 70−74 °C/0.05 mmHg; ^1H-NMR (60 MHz, $CDCl_3$) δ 0.10 (9H, s, Me_3Si); 1.25 (9H, s, $(CH_3)_3C$); 1.64 (3H, s, CH_3CCl); 2.07 (3H, s, $CH_3C{=}N$); 2.28 (2H, t, *J* = 7 Hz, CH_2CH_2O); 3.73 (2H, t, *J* = 7 Hz, CH_2O); ^{13}C-NMR (20 MHz) δ 16.4 ($CH_3C{=}N$); 28.9 (CH_3CCl); 30.1 ($(CH_3)_3C$); 44.4 (CH_2CH_2O); 54.9 ($C(CH_3)_3$); 59.4 (CH_2O); 76.3 (CCl); 163.9 (C=N); IR (NaCl) 1663 cm^{-1} (C=N); MS (70 eV) *m*/*z* (%) no M^+, 206/8(2); 151/3(23); 119(10); 105(16); 98(21); 77(18); 57(100). Anal. Calcd for $C_{13}H_{28}ClNOSi$: C, 56.18; H, 10.16; N, 5.04. Found: C, 56.04; H, 10.23; N, 4.96.

Synthesis of *cis*-2-Alkoxy-3-(*N*-alkylamino)-2,3-dimethyloxolanes hydrochlorides (3a−f). A solution of imine **2** (3 mmol) in the alcohol (R^2OH; 10 mL) was stirred under reflux for 2 h. The alcohol was evaporated *in vacuo*, and the solid residue was washed with ice-cooled dry ether (2

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× 5 mL). After evaporation of traces of the solvent *in vacuo*, the crude hydrochloride **3** was obtained as crystals and used without further purification in the next step (Table 1).

***cis*-3-(*N*-Isopropylamino)-2-methoxy-2,3-dimethyloxolane hydrochloride (3a):** mp 106−107 °C; ^{1}H-NMR (270 MHz) δ 1.57 and 1.59 (2 × 3H, 2 × d, J = 6.4 Hz, CH(CH_3)$_2$); 1.61 and 1.64 (2 × 3H, 2 × s, CH_3CN and CH_3CO); 2.10−2.22 and 2.64−2.78 (2 × 1H, 2 × m, CH_2CH_2O); 3.33 (3H, s, OCH_3); 3.51 (1H, septet, J = 6.4 Hz, CH(CH_3)$_2$); 3.92 (2H, ∼t, J ∼ 6.3 Hz, CH_2O); 7.4−9.8 (2H, 2 × s, broad, NH. HCl); ^{13}C-NMR (67.9 MHz) δ 16.3, 19.7, 21.6 and 21.9 (CH(CH_3)$_2$, CH_3CN and CH_3CO); 35.7 (CH_2CH_2O); 48.6 (OCH_3); 49.9 (CH); 63.9 (CH_2O); 68.8 (CN); 106.0 (OCO); IR (KBr) 3240−3600 cm^{-1} (NH); 1384; 1153; 1034 and 1021 cm^{-1}. Anal. Calcd for $C_{10}H_{22}ClNO_2$: C, 53.68; H, 9.91; N, 6.26. Found: C, 53.79; H, 10.05; N, 6.11.

***cis*-2-Ethoxy-3-(*N*-isopropylamino)-2,3-dimethyloxolane hydrochloride (3b):** mp 126−130 °C; ^{1}H-NMR (270 MHz) δ 1.25 (3H, t, J = 6.9 Hz, CH_2CH_3); 1.57 and 1.63 (3H, 2 × s, CH_3CN and CH_3CO); 1.59 (6H, d, J = 6.6 Hz, CH(CH_3)$_2$); 2.20 (1H, ABdd, J = 12.2, 7.4, 4.95 Hz, HCHCH$_2$O); 2.76 (1H, ABt, J = 12.2, 8.91 Hz, HCHCH$_2$O); 3.49 (1H, septet, J = 6.6 Hz, CH(CH_3)$_2$); 3.53−3.72 (2H, m, OCH_2CH$_3$); 3.86−3.97 (2H, m, CH$_2$CH_2O); 8.3−9.5 (2H, 2 × s broad, NH. HCl); ^{13}C-NMR (67.9 MHz) δ 15.5 (CH_2CH_3); 17.6 and 19.7 (CH_3CO and CH_3CN); 22.0 and 22.2 (CH(CH_3)$_2$); 36.0 (CH_2CH_2O); 49.7 (CH); 57.0 (OCH_2CH$_3$); 63.9 (CH$_2$CH_2O); 68.9 (CN); 105.6 (OCO); IR (KBr) 1175, 1155, 1060 and 1027 cm^{-1}. Anal. Calcd for $C_{11}H_{24}ClNO_2$: C, 55.57; H, 10.17; N, 5.89. Found: C, 55.60; H, 10.08; N, 5.96.

***cis*-3-(*N*-Cyclohexylamino)-2-methoxy-2,3-dimethyloxolane hydrochloride (3c):** mp 168−170 °C; ^{1}H-NMR (270 MHz) δ 1.18−1.30 and 1.82−2.29 (10H, m, (CH$_2$)$_5$); 1.58 and 1.63 (2 × 3H, 2 × s, CH_3CN and CH_3CO); 1.95−2.30 and 2.59−2.70 (2 × 1H, 2 × m, HCHCH$_2$O); 3.0−3.15 (1H, m, CH); 3.32 (3H, s, OCH_3); 3.92 (2H, ∼dd, J = 8.5, 6.3 Hz, CH_2O); 7.92 and 9.73 (2H, 2 × s broad, NH. HCl); ^{13}C-NMR (67.9 MHz) δ 16.5 and 19.9 (CH_3CO and CH_3CN); 24.5; 25.1; 31.4 and 33.2 ((CH$_2$)$_5$); 35.6 (CH_2CH_2O); 48.6 (OCH_3); 57.0 (CH); 63.9 (CH_2O); 68.8 (CN); 105.8 (OCO); IR (KBr) 3160−3500 cm^{-1} (NH); 1160; 1130; 1115; 1055 and 1027 cm^{-1}. Anal. Calcd for $C_{13}H_{26}ClNO_2$: C, 59.19; H, 9.93; N, 5.31. Found: C, 59.31; H, 9.80; N, 5.24.

***cis*-3-(*N*-*sec*-Butylamino)-2-methoxy-2,3-dimethyloxolane hydrochloride (3d):** mp 105−108 °C; ^{1}H-NMR (270 MHz) δ 1.01 and 1.03 (total 3H, 2 × t, J = 7.42 Hz, $CHCH_2CH_3$); 1.58−1.64 (3H, m, CHCH_3); 1.62 and 1.63 (6H, 2 × s, CH_3CO and CH_3CN); 1.84−2.18 (2H, m, CHCH_2CH$_3$); 2.21−2.28 (1H, m, HCHCH$_2$O); 2.43−2.70 (1H, m, HCHCH$_2$O); 3.10−3.27 (1H, m, CHCH$_3$); 3.33 and 3.34 (3H, 2 × s, OCH_3); 3.89−3.98 (2H, m, CH_2O); 7.01 and 8.91 (2H, 2 × s broad, NH·HCl); ^{13}C-NMR (67.9 MHz) δ 10.6 and 10.6 ($CHCH_2CH_3$); 16.0 and 16.7; 18.3; 18.6; 19.6 and 20.0 (CHCH_3, CH_3CN and CH_3CO); 28.3 and 29.0 (CHCH_2CH$_3$); 34.9 and 35.9 (CH_2CH_2O); 48.6 and 48.9 (OCH_3); 55.2 and 55.9 (CHCH$_3$); 63.9 and 64.0 (CH_2O); 68.9 (CN); 105.7 and 106.2 (OCO); IR (KBr) 3160−3660 (NH); 1165; 1130 and 1027 cm^{-1}. Anal. Calcd for $C_{11}H_{24}ClNO_2$: C, 55.57; H, 10.17; N, 5.89. Found: C, 55.62; H, 10.09; N, 5.99.

***cis*-3-(*N*-*sec*-Butylamino)-2-ethoxy-2,3-dimethyloxolane hydrochloride (3e):** mp 96−100 °C; ^{1}H-NMR (270 MHz) δ 1.01 and 1.03 (total 3H, 2 × t, J = 6.6 Hz, $CHCH_2CH_3$); 1.22 and 1.24 (3H, 2 × t, J = 6.9 Hz, OCH_2CH_3); 1.55 and 1.67 (6H, 2 × s, CH_3CO and CH_3CN); 1.58−1.64 (3H, m, CHCH_3); 1.82−1.95 (2H, m, CHCH_2CH$_3$); 1.99−2.31 (1H, m, HCHCH$_2$O); 2.50−2.81 (1H, m, HCHCH$_2$O); 3.11−3.25 (1H, m, CHCH$_3$); 3.52−3.72 (2H, m, OCH_2CH$_3$); 3.89−3.97 (2H, m, CH$_2$CH_2O); 8.86 and 9.29 (2H, 2 × s broad, NH·HCl); ^{13}C-NMR (67.9 MHz) δ 10.5 and 10.6 ($CHCH_2CH_3$); 15.4 and 15.5; 16.9 and 17.8 (OCH_2CH_3 and CHCH_3); 18.6 and 18.7; 19.7 and 19.9 (CH_3CN and CH_3CO); 28.6 and 29.1 (CHCH_2CH$_3$); 35.0 and 36.3 (CH_2CH_2O); 55.0 and 55.9 (CHCH$_3$); 57.0 and 57.1 (OCH_2CH$_3$); 63.9 and 64.0 (CH_2CH_2O); 68.8 and 68.9 (CN); 105.4 and 106.1 (OCO); IR (KBr) 3260−3640 (NH); 1155; 1130; 1050 and 1025 cm^{-1}. Anal. Calcd for $C_{12}H_{26}ClNO_2$: C, 57.24; H, 10.41; N, 5.56. Found: C, 57.39; H, 10.53; N, 5.49.

***cis*-3-(*N*-*sec*-Butylamino)-2,3-dimethyl-2-propoxyoxolane hydrochloride (3f):** mp 67−72 °C; ^{1}H-NMR: (270 MHz) δ 0.93 (total 3H, t, J = 7.25 Hz, $OCH_2CH_2CH_3$); 1.01 and 1.04 (3H, 2 × t, J = 7.1 Hz, $CHCH_2CH_3$); 1.31−1.39 (2H, m, CH_2CH); 1.56; 1.57; 1.57 and 1.62 (total 6H, 4 × s, CH_3CO and CH_3CN); 1.62−1.68 (3H, m, CHCH_3); 1.82−2.15 (2H, m, $OCH_2CH_2CH_3$); 2.24−2.71 (2H, m, NCCH_2CH$_2$O); 3.11−3.22 (1H, m, CHCH$_2$CH$_3$); 3.46−3.64 (2H, m, OCH_2CH$_2$CH$_3$); 3.89−3.98 (2H, m, NCCH$_2$CH_2O); 7.12, 8.52, 9.12, 10.60 (2H, s broad, NH·HCl); ^{13}C-NMR (67.9 MHz) δ 10.4 and 10.5 ($CHCH_2CH_3$); 13.8 ($OCH_2CH_2CH_3$); 16.7 and 17.6 (CH_3CH); 18.5; 18.7; 19.5 and 19.9 (CH_3CO and CH_3CN); 19.4 and 19.4 ($OCH_2CH_2CH_3$); 28.5 and 29.0 (CHCH_2CH$_3$); 34.8 and 36.1 (NCCH_2CH$_2$O); 55.1 and 56.0 (CHCH$_2$CH$_3$); 61.2 and 61.9 ($CH_3CH_2CH_2O$); 63.9 and 64.1 (NCCH$_2$CH_2O); 68.9 (CN); 105.4 and 106.1 (CO); IR (KBr) 3300−3500 cm^{-1} (NH), 1155; 1130 and 1026 cm^{-1}. Anal. Calcd for $C_{13}H_{28}ClNO_2$: C, 58.74; H, 10.62; N, 5.27. Found: C, 58.86; H, 10.72; N, 5.18.

X-ray Crystallographic Analysis of *cis*-3-(*N*-Isopropylamino)-2-methoxy-2,3-dimethyloxolane Hydrochloride (3a).[8] Pure crystals were obtained by recrystallization from methanol/diethyl ether (−20 °C). The principal crystallographic parameters of compound **3a** are as follows:[8] monoclinic; M_r = 223.74; $P2_1/c$; a = 6.462(2); b = 11.041(4); c = 17.627(4) Å; β = 98.82(3)°; ν = 1242.8(6) Å^3; Z = 4; D_x = 1.196 g cm^{-3}; Mo Kα; λ = 0.71069 Å; μ = 2.87 cm^{-1}; F(000) = 488; T = 293 K; final R_1 = 0.0541, ωR_2 = 0.1422 for 2428 reflections with $I > 2\sigma(I)$; all data R_1 = 0.0881 and ωR_2 = 0.1697.

Synthesis of *cis*-2-Alkoxy-3-(*N*-alkylamino)-2,3-dimethyloxolanes (4a−f). Hydrochloride **3** (2 mmol) was dissolved in dichloromethane (10 mL) and poured into a 1 N aqueous potassium carbonate solution (30 mL). The mixture was thoroughly shaken, the organic layer was separated, and the water phase was extracted two more times with dichloromethane (2 × 10 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo* to give the pure *cis*-2-alkoxy-3-aminooxolanes **4** (Table 1).

***cis*-3-(*N*-Isopropylamino)-2-methoxy-2,3-dimethyloxolane (4a):** ^{1}H-NMR (270 MHz) δ 1.07 and 1.08 (2 × 3H, 2 × d, J = 6.3 Hz, CH(CH_3)$_2$); 1.14 and 1.26 (2 × 3H, 2 × s, CH_3CO and CH_3CN); 1.69 (1H, s broad, NH); 1.85−2.06 (2H, m, CH_2CH$_2$O); 2.93 (1H, septet, J = 6.3 Hz, CH(CH_3)$_2$); 3.22 (3H, s, OCH_3); 3.76−3.83 (2H, m, CH_2O); ^{13}C-NMR (67.9 MHz) δ 14.9 and 22.6 (CH_3CN and CH_3CO); 25.7 and 26.1 (CH(CH_3)$_2$); 38.1 (CH_2CH_2O); 44.3 (CH(CH$_3$)$_2$); 48.2 (OCH_3); 64.1 (CH_2O); 65.9 (CN); 106.9 (OCO); IR (NaCl) 3140−3390 (NH); 1370; 1165; 1130; 1100 and 1045 cm^{-1}; MS (70 eV) m/z (%) 187 (M$^+$; 4); 156(22); 113(51); 98(69); 84(49); 70(38); 58(33); 42(100). Anal. Calcd for $C_{10}H_{21}NO_2$: C, 64.13; H, 11.30; N, 7.48. Found: C, 64.19; H, 11.20; N, 7.56.

***cis*-2-Ethoxy-3-(*N*-isopropylamino)-2,3-dimethyloxolane (4b):** ^{1}H-NMR (270 MHz) δ 1.07 and 1.08 (2 × 3H, 2 × d, J = 6.4 Hz, CH(CH_3)$_2$); 1.14 and 1.27 (2 × 3H, 2 × s, CH_3CO and CH_3CN); 1.15 (3H, t, J = 6.9 Hz, CH_2CH_3); 1.68 (1H, s broad, NH); 1.83−2.08 (2H, m, CH_2CH$_2$O); 2.93 (1H, septet, J = 6.2 Hz, CH(CH$_3$)$_2$); 3.41−3.61 (2H, m, CH_2CH$_3$); 3.76−3.81 (2H, m, CH$_2$CH_2O); ^{13}C-NMR (67.9 MHz) δ 15.9 and 22.5 (CH_3CO, CH_2CH_3 and CH_3CN); 25.8 and 26.1 (CH(CH_3)$_2$); 38.3 (CH_2CH_2O); 44.2 (CH); 55.8 (OCH_2CH$_3$); 64.0 (CH$_2$CH_2O); 65.7 (CN); 106.6 (OCO); IR (NaCl) 3140−3360 (NH); 1373; 1168; 1132; 1128; 1100 and 1055 cm^{-1}; MS (70 eV) m/z (%) 201 (M$^+$; 3); 156(35); 113(67); 98(92); 84(62); 58(33); 42(100). Anal. Calcd for $C_{11}H_{23}NO_2$: C, 65.63; H, 11.52; N, 6.96. Found: C, 65.46; N, 11.59; N, 6.88.

***cis*-3-(*N*-Cyclohexylamino)-2-methoxy-2,3-dimethyloxolane (4c):** ^{1}H-NMR (270 MHz) δ 1.02−1.33 and 1.56−2.05 (12H, m, (CH$_2$)$_5$ and CH_2CH$_2$O); 1.13 and 1.25 (2 × 3H, 2 × s, CH_3CO and CH_3CN); 1.88 (1H, s broad, NH); 2.42−2.52 (1H, m, CH); 3.22 (3H, s, OCH_3); 3.75−3.81 (2H, m, CH_2O); ^{13}C-NMR (67.9 MHz) δ 14.8 and 22.8 (CH_3CO and CH_3CN); 25.8; 36.4; 36.8 and 38.3 ((CH$_2$)$_5$ and CH_2CH$_2$O); 48.1 (OCH_3); 52.3 (CH); 64.0 (CH$_2$CH_2O); 65.6 (CN); 106.8 (OCO); IR (NaCl) 3050−3380 (NH); 1135; 1123 and 1055 cm^{-1}; MS (70 eV) m/z (%) 227 (M$^+$; 3); 153(40); 124(44); 98(24); 83(34); 72(100); 55(34). Anal. Calcd for $C_{13}H_{25}NO_2$: C, 68.68; H, 11.08; N, 6.16. Found: C, 68.76; H, 11.04; N, 6.24.

***cis*-3-(*N*-*sec*-Butylamino)-2-methoxy-2,3-dimethyloxolane (4d):** ^{1}H-NMR (270 MHz) δ 0.89 (3H, t, J = 7.4 Hz, $CHCH_2CH_3$); 1.04 and 1.06 (total 3H, 2 × d, J = 6.1 Hz, $CHCH_3$); 1.11 and 1.15; 1.25 and 1.26 (total 6H, 2 × s, CH_3CO and CH_3CN); 1.29−1.53 (2H, m, $CHCH_2CH_3$); 1.77−1.93 (2H, m, CH_2CH_2O); 1.94−2.08 (1H, m, NH); 2.62 (1H, sextet, J = 6.1 Hz, $CHCH_3$); 3.22 and 3.23 (3H, s, OCH_3); 3.79 (2H, d, J = 9.2, 5.9 Hz, CH_2O); NH invisible; ^{13}C-NMR (67.9 MHz) δ 11.0 ($CHCH_2CH_3$); 14.6; 14.8; 22.4; 23.0; 23.1 and 23.5 (CH_3CH, CH_3CO and CH_3CN); 32.0 and 32.5 ($CHCH_2CH_3$); 37.8 and 38.4 (CH_2CH_2O); 48.1 and 48.1 (OCH_3); 49.8 and 50.4 ($CHCH_2CH_3$); 64.1 and 64.2 (CH_2O); 65.4 and 65.9 (CN); 106.9 and 107.0 (OCO); IR (NaCl) 3350 (CNH); 1373; 1155; 1130; 1105 and 1050 cm^{-1}; MS (70 eV) *m*/*z* (%) 201 (M^+; 1); 127(30); 112(27); 98(100); 97(31); 72(35); 70(28). Anal. Calcd for $C_{11}H_{23}NO_2$: C, 65.63; H, 11.52; N, 6.96. Found: C, 65.79; H, 11.59; N, 6.83.

3-(*N*-*sec*-Butylamino)-2-ethoxy-2,3-dimethyloxolane (4e): ^{1}H-NMR (270 MHz) δ 0.89 (3H, t, J = 7.3 Hz, $CHCH_2CH_3$); 1.05−1.17 (6H, m, CH_3CH and OCH_2CH_3); 1.14; 1.26 and 1.27 (6H, 2 × s, CH_3CN and CH_3CO); 1.29−1.60 (2H, m, $CHCH_2CH_3$); 1.80−1.90 and 1.99−2.10 (2H, m, CH_2CH_2O); 1.85 (1H, s broad, NH); 2.58−2.65 (1H, m, CH); 3.43−3.61 (2H, m, OCH_2CH_3); 3.76−3.82 (2H, m, CH_2CH_2O); ^{13}C-NMR (67.9 MHz) δ 11.0 ($CHCH_2CH_3$); 15.8; 15.8; 22.3; 23.1; 23.1 and 23.7 (OCH_2CH_3, $CHCH_3$, CH_3CN and CH_3CO); 32.0 and 32.6 ($CHCH_2CH_3$); 37.8 and 38.5 (CH_2CH_2O); 49.8 and 50.5 ($CHCH_3$); 55.8 (OCH_2CH_3); 64.1 and 64.1 (CH_2CH_2O); 65.4 and 65.9 (CN); 106.6 and 106.7 (OCO); IR (NaCl) 3355 (NH) 1165; 1110 and 1055 cm^{-1}; MS (70 eV) *m*/*z* (%) 215 (M^+; 2); 170(30); 127(39); 126(31); 112(27); 98(100); 70(29). Anal. Calcd for $C_{12}H_{25}NO_2$: C, 66.93; H, 11.70; N, 6.50. Found: C, 66.98; H, 11.61; N, 6.63.

3-(*N*-*sec*-Butylamino)-2,3-dimethyl-2-propoxyoxolane (4f): ^{1}H-NMR (270 MHz) δ 0.89 (3H, t, J = 7.4 Hz, CH_2CH_3); 0.92 (3H, t, J = 7.24 Hz, CH_2CH_3); 1.04 and 1.06 (total 3H, 2 × d, J = 6.28 Hz, $CHCH_3$); 1.11; 1.14; 1.26 and 1.28 (6H, 4 × s, CH_3CO and CH_3CN); 1.30−1.56 (5H, m, $CHCH_2CH_3$, $OCH_2CH_2CH_3$ and NH); 1.79−2.10 (2H, m, CCH_2CH_2O); 1.83 (1H, s broad, NH); 2.57−2.66 (1H, m, $CHCH_3$); 3.36−3.54 (2H, m, $OCH_2CH_2CH_3$); 3.73−3.82 (2H, m, CCH_2CH_2O); ^{13}C-NMR (67.9 MHz) δ 11.0 and 14.0 (CH_2CH_3); 15.7; 22.4; 23.1; 23.2 and 23.7 (CH_3CO, $CHCH_3$ and CH_3CN); 19.6 ($OCH_2CH_2CH_3$); 32.4 and 32.6 ($CHCH_2CH_3$); 37.8 and 38.5 (CCH_2CH_2O); 49.8 and 50.5 ($CHCH_3$); 59.9 and 60.0 ($OCH_2CH_2CH_3$); 64.1 and 64.1 (CCH_2CH_2O); 65.5 and 66.0 (CN); 106.6 (OCO); IR (NaCl) 3355 (NH) 1375, 1165, 1135, and 1110 cm^{-1}; MS (70 eV) *m*/*z* (%) no M^+; 200 ($M^+ - CH_2CH_3$, 1); 170(15); 112(24); 98(87); 97(56); 72(44); 55(66); 41(100). Anal. Calcd for $C_{13}H_{27}NO_2$: C, 68.08; H, 11.87; N, 6.11. Found: C, 67.94; H, 11.94; N, 6.19.

Reaction of α-Chloro-γ-((trimethylsilyl)oxy)ketimines 2 with an Alcohol in the Presence of Potassium Carbonate. To a solution of α-chloroimine **2** (15 mmol) in the dry alcohol (40 mL) was added potassium carbonate (6.21 g, 45 mmol). The solution was refluxed for a period indicated in Table 2 and then cooled, poured into an ice cooled solution of 0.5 N aqueous sodium hydroxide (100 mL), and extracted with dichloromethane (3 × 60 mL). After drying of the combined extracts with potassium carbonate and evaporation of the solvent *in vacuo*, the mixture of *cis*- and *trans*-2-alkoxy-3-aminooxolanes **4** and **14** was distilled *in vacuo* (Table 2). The spectral data of the *trans*-3-amino-2-alkoxyoxolanes **14** were deduced from the spectral data of the mixture of *cis*- and *trans*-stereoisomers **4** and **14**.

***trans*-3-(*N*-Isopropylamino)-2-methoxy-2,3-dimethyloxolane (14a):** ^{1}H-NMR (270 MHz) δ 1.06 (6H, d, J = 6.3 Hz, $CH(CH_3)_2$); 1.15 (1H, s broad, NH); 1.16 and 1.28 (2 × 3H, 2 × s, CH_3CO and CH_3CN); 1.90−2.03 (2H, m, CH_2CH_2O); 2.92 (1H, septet, J = 6.3 Hz, $CH(CH_3)_2$); 3.23 (3H, s, OCH_3); 3.68−3.87 (2H, m, CH_2O); ^{13}C-NMR (67.9 MHz) δ 14.1 and 19.2 (CH_3CO and CH_3CN); 26.4 and 26.8 ($CH(CH_3)_2$); 33.9 (CH_2CH_2O); 43.4 ($CH(CH_3)_2$); 48.2 (OCH_3); 66.6 (CN); 109.4 (OCO).

***trans*-3-(*N*-Isopropylamino)-2,3-dimethyl-2-ethoxyoxolane (14b):** ^{1}H-NMR (60 MHz) δ 1−1.3 (15H, m, $CH(CH_3)_2$, CH_3CO, CH_3CN, CH_3CH_2); 1.8 (1H, s broad, NH); 1.8−2.2 (2H, m, CH_2CH_2O); 2.97 (1H, septet, J = 6 Hz, $CH(CH_3)_2$); 3.47 (2H, q, J = 7 Hz, CH_2CH_3); 3.76 (2H, t, J = 6.5 Hz, CH_2CH_2O); ^{13}C-NMR (20 MHz) 14.9; 15.9; 19.2; 26.4 and 26.8 (CH_3CO, CH_3CN, CH_3CH_2, and $(CH_3)_2CH$); 33.9 (CH_2CH_2O); 43.4 (CH); 55.8 (OCH_2CH_3); 64.3 (OCH_2CH_2); 66.6 (CN); 109.2 (OCO).

***trans*-3-(*N*-Cyclohexylamino)-2,3-dimethyl-2-methoxyoxolane (14c):** ^{1}H-NMR (270 MHz) δ 1.04−1.36 and 1.70−1.91 (10H, m, $(CH_2)_5$); 1.14 and 1.28 (2 × 3H, 2 × s, CH_3CO and CH_3CN); 1.95 (2H, t, J = 7.6 Hz, CH_2CH_2O); 2.38−2.47 (1H, m, CH); 3.20 (3H, s, OCH_3); 3.70−3.89 (2H, m, CH_2O); NH invisible; ^{13}C-NMR (67.9 MHz) 14.0 and 19.3 (CH_3CO and CH_3CN); 25.6, 37.0 and 37.6 ($(CH_2)_5$); 33.9 (CH_2CH_2O); 48.1 (OCH_3); 51.5 (CH); 64.3 (CH_2O); 66.6 (CN); 109.4 (OCO).

***cis*- and *trans*-3-(*N*-Cyclohexylamino)-2,3-dimethyl-2-ethoxyoxolane 4g and 14g** (ratio 2/3). ^{1}H-NMR (270 MHz) δ 1.11 and 1.14 (total 3H, 2 × t, J = 6.9 Hz, OCH_2CH_3); 1.12, 1.15, 1.27, and 1.28 (6H, 4 × s, CH_3CO and CH_3CN); 1.08−1.16, 1.20−1.32, 1.43−1.79 (10H, m, $(CH_2)_5$); 1.80−2.10 (2H, m, CH_2CH_2O); 2.37−2.52 (1H, m, CH); 3.40−3.60 (2H, m, OCH_2CH_3); 3.70−3.84 (2H, m, CH_2CH_2O); NH invisible; ^{13}C-NMR (67.9 MHz) δ 14.8, 15.8, 19.3, and 22.6 (OCH_2CH_3, CH_3CO and CH_3CN); 25.8, 25.9, 36.5, 36.9, 37.6 and 38.3 ($(CH_2)_5$); 33.9 (CH_2CH_2O); 51.5 and 52.4 (CH); 55.7 and 55.8 (OCH_2CH_3); 64.0 and 64.3 (CH_2CH_2O); 65.6 and 66.6 (CN); 106.5 and 109.1 (OCO); IR (NaCl) 3345 (NH), 1450, 1375, 1150, 1130, 1060 and 1005 cm^{-1}; MS (70 eV) *m*/*z* (%) no M^+; 212 ($M^+ - CH_2CH_3$; 6); 196(30); 153(46); 124(47); 98(37); 72(100); 70(38). Mass spectra of isomers **4g** and **14g** were identical.

***cis*- and *trans*-3-(*N*-*tert*-Butylamino)-2,3-dimethyl-2-methoxyoxolane 4h/14h** (ratio 3/2): ^{1}H-NMR (60 MHz) δ 1.14 and 1.17 (total 9H, 2 × s, $(CH_3)_3C$); 1.16, 1.19, 1.24 and 1.26 (6H, 4 × s, CH_3CO and CH_3CN); 1.5 (1H, s broad, NH); 1.7−2.3 (2H, m, CH_2CH_2O); 3.17 (3H, s, OCH_3); 3.6−4.1 (2H, m, CH_2O); ^{13}C-NMR (20 MHz) 13.9, 14.2, 20.2 and 23.9 (CH_3CO and CH_3CN); 32.6 and 32.8 ($(CH_3)_3C$); 36.1 and 39.6 (CH_2CH_2O); 48.0 and 48.2 (OCH_3); 50.5 and 51.0 ($C(CH_3)_3$); 64.2 and 64.6 (CH_2O); 65.6 and 65.9 (CHCN); 108.1 and 110.1 (OCO); IR (NaCl) 3460 (NH) and 2825 cm^{-1} (OMe); MS (70 eV) *m*/*z* (%) 201 (M^+; 1); 127(36); 112(36); 72(42); 71(60); 70(84); 57(100). Isomers **4h** and **14h** were not separated by capillary GC.

***cis*-3-(*N*-*tert*-Butylamino)-2-ethoxy-2,3-dimethyloxolane (4i):** ^{1}H-NMR (60 MHz) 1.13 (9H, s, $(CH_3)_3$); 1.10 (3H, t, J = 7 Hz, CH_3CH_2); 1.2 and 1.25 (2 × 3H, 2 × s, CH_3CN and CH_3CO); 1.6−2.3 (2H, m, CH_2CH_2O); 3.47 (2H, q, J = 7 Hz, OCH_2CH_3); 3.75 (2H, dd, J = 8.5, 6 Hz, CH_2CH_2O); NH invisible; ^{13}C-NMR (20 MHz): 14.8 and 23.8 (CH_3CN and CH_3CO); 15.9 (CH_3CH_2); 32.6 ($(CH_3)_3C$); 39.9 (CH_2CH_2O); 50.6 ($C(CH_3)_3$); 55.7 (CH_2CH_3); 64.6 (CH_2CH_2O); 65.6 (CH_3CN); 108.0 (OCO); IR (NaCl) 3460 cm^{-1} (NH); MS (70 eV) *m*/*z* (%) 215 (M^+; 0.2); 163(8); 112(23); 98(19); 97(14); 70(56); 62(98); 57(100).

Reaction of α-Chloro-γ-((trimethylsilyl)oxy)ketimine (2a) with Sodium Methoxide in Methanol. To α-chloroimine **2a** (0.66 g, 2.5 mmol) at room temperature was added a 2 N solution of sodium methoxide in methanol (37.5 mL, 7.5 mmol). The stirred solution was refluxed for 2 h and then cooled, poured into 0.5 N aqueous sodium hydroxide (30 mL), and extracted with dichloromethane (3 × 20 mL). After drying of the combined extracts with magnesium sulfate and evaporation of the solvent *in vacuo*, a mixture of the 2-alkoxy-3-aminooxolanes *cis*-**4a** and *trans*-**14a** (ratio *c*/*t*: 12/88) was obtained in quantitative yield (Table 2).

Isomerization of *trans*-14a to *cis*-4a. Through a solution of *trans*-**14a** and *cis*-**4a** (*c*/*t*: 12/88; 0.20 g, 1.1 mmol) in dry methanol (5 mL) was bubbled dry HCl during 5 min. After the solution was refluxed for 2 h, the solvent was removed *in vacuo* and the residue dissolved in dichloromethane (5 mL) and poured into a 1 N aqueous potassium carbonate solution (15 mL). After vigorous shaking, the organic layer was separated and the water phase extracted two more times with dichloromethane (2 × 5 mL). After drying ($MgSO_4$) and evaporation of the solvent, pure *cis*-**4a** (0.18 g, yield 90%) was obtained, containing no detectable amount of *trans*-**14a**.

3-(*N*-Alkylamino)-3-methyl-2-methyleneoxolanes (15). Upon preparative gas chromatography of the *cis*/*trans* mixtures **4a**/**14a** (ratio 3/5) and **4h**/**14h** (ratio 3/2), obtained by reaction of imines **2a** and **2d** with potassium carbonate in methanol (*vide supra*), the 2-methyleneoxolanes **15** were isolated in quantitative yield.

3-(*N*-Isopropylamino)-3-methyl-2-methyleneoxolane (15a): ^{1}H-NMR (270 MHz) δ 1.07 and 1.08 (2 × 3H, 2 × d, J = 6.4 Hz, CH(CH_3)$_2$); 1.34 (3H, s, CH_3CN); 1.45 (1H, s broad, NH); 1.89 (1H, AB, J = 12.2 Hz, HCHCH$_2$O); 2.05−2.20 (1H, m, HCHCH$_2$O); 2.94 (1H, septet, J = 6.4 Hz, CH); 3.89 and 4.21 (2 × 1H, 2 × d, J = 1.98 Hz, =CH$_2$); 4.03 (1H, ABdd, J = 8.57, 7.26, 6.26 Hz, HCHO); 4.16 (1H, ABdd, J = 8.57, 7.26, 6.60 Hz, HCHO); ^{13}C-NMR (20 MHz) 26.0 (CH$_3$CN); 26.1 ((CH$_3$)$_2$CH); 38.4 (CH$_2$CH$_2$O); 44.0 ((CH$_3$)$_2$$C$H); 61.7 (CH$_3$$C$N); 67.1 (CH$_2$O); 78.2 (=CH$_2$); 168.5 (O$C$=CH$_2$); IR (NaCl) 3320 (NH), 1664, 1376, 1042 cm^{-1}. MS (70 eV) m/z (%) 155 (M$^+$, 1); 140 (M$^+$ − CH$_3$; 10); 112(27); 98(93); 97(47); 84(39); 70(33); 58(100). Anal. Calcd for $C_9H_{17}NO$: C, 69.63; H, 11.04; N, 9.02. Found: C, 69.71; H, 11.00; N, 9.06.

3-(*N*-*tert*-Butylamino)-3-methyl-2-methyleneoxolane (15b): ^{1}H-NMR (60 MHz) δ 1.18 (9H, s, (CH$_3$)$_3$C); 1.38 (3H, s, CH$_3$CN); 1.6 (1H, s broad, NH); 1.9−2.2 (2H, m, CH_2CH$_2$O); 3.8−4.2 (2H, m, OCH$_2$); 4.0 and 4.14 (2 × 1H, ABm, J = 8.4 Hz, CH$_2$=C); ^{13}C-NMR (20 MHz) 28.0 (CH$_3$CN); 32.3 ((CH$_3$)$_3$C); 41.0 (CH$_2$CH$_2$O); 51.6 (C(CH$_3$)$_3$); 61.3 (CH$_3$$C$N); 67.3 (CH$_2$O); 78.2 (CH$_2$=); 171.2 (O$C$=CH$_2$); IR (NaCl) 1671 cm^{-1} (CH$_2$=C); MS (70 eV) m/z (%) 169 (M$^+$; 20); 97(16); 96(12); 70(40); 58(100); 57(48).

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