Deprotonation of Oxazolinyloxiranes: Formation of Substituted Acyloxiranes

Saverio Florio,*[a] Vito Capriati,[a] Serena Di Martino,[a] and Alessandro Abbotto[b]

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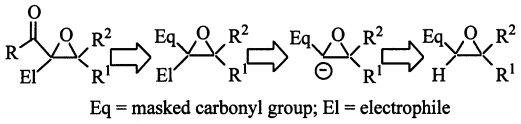
Deprotonation of oxazolinyloxiranes **1a**, **1h**, and **1k** with *s*BuLi/TMEDA at –100 °C in Et_2O furnishes oxazolinyloxiranyllithium compounds[1] **1b**, **1i**, and **1l** which are stable at low temperature and can be trapped with electrophiles to give substituted oxiranes **1c–1g** and **1j**. The reaction of **1b** with aldehydes produced diastereomers *syn* (**2a–d**) and *anti* (**3a–d**). Oxiranyllithium **1i** from *trans*-1-(4,4-dimethyl-2-oxazolinyl)-2-*p*-tolylepoxy-ethane (**1h**) was found to be configurationally stable while oxiranyllithium **1l**, generated from the *cis* isomer **1k**, was not. Oxazolinylepoxides **1d**, **1j**, and **1m** could be deblocked to acyloxiranes **5a–e** through oxazolidines **4a–e**.

α,β-Epoxy aldehydes and ketones are particularly attractive intermediates to be used for synthetic purposes. Indeed, the elaboration of the epoxy moiety or the carbonyl function or both, has allowed the preparation of a number of useful compounds such as vinyl iodides,[2] α,β-unsaturated aldehydes,[3] butyrolactones and furanones,[4] β-lactam antibiotics via chiral α,β-epoxyimines,[5] chiral β,γ-epoxy alcohols,[6a−6d] 1,2- and 1,3-diols,[7a] 1,2,3-triols,[7b] 1,2-cyclohexanediols,[8] aldols,[9a] and 1,3-cyclohexanediols,[9b] hydroxy-substituted tetrahydrofurans,[10] 2-deoxyhexoses.[11]

α,β-Epoxy aldehydes and ketones are usually prepared by oxidation of epoxy alcohols.[5,6a,9a,12,13] An alternative route relies upon the epoxidation of α,β-unsaturated carbonyl compounds.[7a,14a−14e] An asymmetric synthesis of optically active α,β-epoxy aldehydes from α,β-unsaturated acids has also been described.[15]

Among the many routes to substituted epoxides now available, one method which has not yet been fully developed is the coupling reaction of oxiranyl anions with electrophiles. Such a strategy relies on the presence on the epoxide moiety of functional groups capable of stabilizing the carbanionic species that can be generated by deprotonation of simpler derivatives. Some oxiranyllithium compounds have been reported as synthetically useful in the functionalization of oxiranes.[16a−16i]

We have recently reported an efficient synthesis of formyl epoxides based on the preparation of oxazolinyl epoxides and subsequent elaboration of the oxazolinyl moiety to the formyl group.[17] The deprotonation−alkylation sequence of α,β-epoxy carbonyl groups as a route to more functionalized derivatives, of course, is not practicable in view of the fact that metallating agents would attack the carbonyl function. We envisaged that, perhaps, such a strategy could be applied to epoxides bearing masked carbonyl groups as illustrated in the retrosynthetic approach of Scheme 1.



Scheme 1. Retrosynthetic approach

In the present paper we report on a novel synthesis of substituted acyloxiranes based on the deprotonation−alkylation−deblocking sequence of certain oxiranyloxazolines.

Results and Discussion

When treated with *s*BuLi/TMEDA in Et_2O at −100°C, the oxiranyloxazoline **1a**, prepared from 2-chloromethyl-4,4-dimethyl-2-oxazoline according to a method described in ref.[17], underwent rapid lithiation which was complete in a few minutes to generate **1b**, which turned out to be stable and could be trapped with Me_3SiCl to give **1c**. The reaction of **1a** with lithium diisopropylamide (LDA) in THF and Me_3SiCl gave a much lower yield of **1c** (27%). The alkylation of **1b** with MeI and allyl bromide led to compounds **1d** and **1e**, respectively, in good yields. Furthermore, the reaction of **1a** with *s*BuLi/TMEDA followed by the addition of acetone and cyclohexanone afforded epoxy alcohols **1f** and **1g**, respectively (Table 1).

The coupling reaction of **1b** with acetaldehyde furnished diastereomeric hydroxyethyl oxazolinyl epoxides **2a** and **3a** as a 1.3:1 mixture (Table 2) which could be easily separated by column chromatography. The isomer **2a**, which was assigned the *syn* configuration (see below), had a less polar character than the *anti* isomer **3a** (ΔR_f = 0.37 on TLC, petroleum ether/AcOEt, 7:3). This could be tentatively explained in terms of intramolecular hydrogen bonds between the OH and the epoxy groups.[18] The intramolecularly associated conformation of the *syn* isomer **2a** should be more easily attainable than the hydrogen-bonded conformation of the *anti* isomer **3a**, for steric reasons. These consider-

[a] Centro C.N.R. "M.I.S.O.", Dipartimento Farmaco-Chimico, Università di Bari,
Via E. Orabona 4, I-70126 Bari, Italy
E-mail: florio@farmchim.uniba.it
[b] Dipartimento di Scienza dei Materiali, II Università degli Studi di Milano − Bicocca,
Via Emanueli 15, I-20126 Milano, Italy

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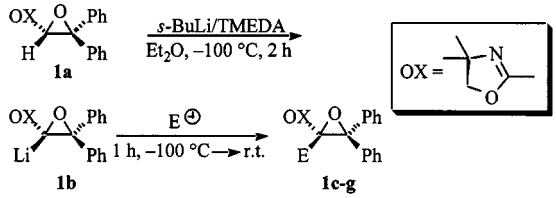
Table 1. Deprotonation of **1a** and reaction with electrophiles



E	Compound	Conversion (%)[a]	Yield (%)[b]
$(CH_3)_3Si$	**1c**	> 95	95
CH_3	**1d**	> 95	62
$CH_2=CHCH_2$	**1e**	69	76
$(CH_3)_2COH$	**1f**	62	67
$(CH_2)_5COH$	**1g**	70	79

[a] This value arises from the following ratio: (initial reacting moles − residual moles)/initial reacting moles. − [b] Based on converted material.

ations are supported by the infrared spectral data of the OH group at high dilution ($5.0 \cdot 10^{-3}$ M, where intermolecular hydrogen bonds are supposed not to take place). The *syn* isomer **2a** showed a broad strongly bonded OH band at 3411 cm^{-1}. No frequence shift was observed at higher concentrations (10^{-2} and 10^{-1} M). In contrast, the *anti* isomer **3a** gave a significant sharp band at 3616 cm^{-1} ascribed to a free OH group.[18,19] In KBr, the band at 3616 cm^{-1} of **3a** was shifted to 3236 cm^{-1}, while the band at 3411 cm^{-1} of **2a** remained substantially unaffected.

Semiempirical calculations[20] were performed in order to assess the preferred conformations and the relative stabilities of the *syn* and *anti* diastereoisomers **2a** and **3a**. Two local minima were found for the *syn* isomer **2a**, both showing favourable hydrogen-bonding interactions. The two conformations differ very little in energy (heats of formation are −33.1 and −32.4 kcal mol^{-1}), the relative difference being within the usual computational error. The distance between the hydroxy group and the epoxy oxygen atom ranges from 2.6 to 2.8 Å. Two local minima have also been found for the *anti* isomer **3a** (ΔH_f = −32.5 and −32.4 kcal mol^{-1}). Although their energies compare well with those of the *syn* isomer, in this case the distance between the OH group and the epoxy oxygen atom is too large (higher than 3.6 Å) to observe hydrogen bonding. Note that a favourable interaction between the OH group and the oxazolinyl ring was never observed in any of the optimized conformations of the *syn* and *anti* isomers.

We wanted to investigate in more detail the reason for the different behavior of the two diastereoisomers. We approached the study by performing a partial geometry optimization for both the *syn* and *anti* isomers, in which an antiperiplanar arrangement between the oxazolinyl ring and the hydroxy group with respect to the bond linking the two stereogenic centers was imposed. Such a situation should favour the formation of a hydrogen bond between the OH function and the epoxy oxygen atom. The optimized structures obtained are shown in Figure 1. The computation for the *syn* isomer resulted in a new geometry, the energy of which (ΔH_f = −32.3 kcal mol^{-1}) matched perfectly that of the previously obtained minima, showing that this structure belongs to the set of minimum-energy conformations as well. Hydrogen bonding involving the epoxy unit is 2.6 Å; the O−C−C−O torsion angle θ (θ as defined in Figure 1) is about 40°. An analogous partial optimization performed for the *anti* isomer showed similar intramolecular hydrogen bonding (2.5 Å; θ = 45°). However, in this case the computed energy was higher by 2 kcal mol^{-1} than that of the *anti* minimum-energy conformations. In fact, steric hindrance between the methyl group adjacent to the OH function and both the oxazolinyl and one of the phenyl rings (2.6−2.7 Å) is the source of the decreased stability. In other words the stabilizing term coming from a favoured hydrogen bonding is counterbalanced by destabilizing steric factors.

It is known that PM3 calculations predict geometries rather successfully, but underestimate intra- and intermolecular nonbonding interactions. In particular, it has been recently shown[21] that nonbonding intermolecular interactions such as coordination bonds to molecules of solvent are generally computed by the PM3 approach to be smaller by 1−5 kcal mol^{-1} with respect to high-level ab initio calculations which include electron correlation. If we keep this in mind, we can expect the structures showing hydrogen

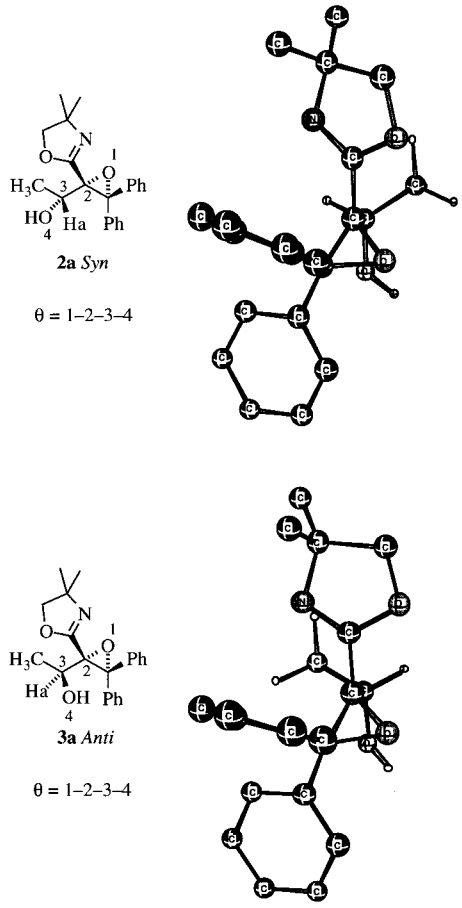


Figure 1. Minimum−energy conformations of the *syn* and *anti* diastereomers **2a** and **3a**

bonding (all of the stable *syn* conformations and the partially optimized *anti* geometry) to have an absolute lower energy than that computed. We can therefore conclude that all of the stable *syn* conformations (one of which is reported in Figure 1) involve hydrogen bonding and have a lower energy with respect to the *anti* diastereoisomer. The hydrogen-bonded *anti* conformation shown in Figure 1 probably compares well with the other minimum-energy *anti* structures, where hydrogen bonding is absent, but is not particularly favoured since it suffers from implicit steric interactions.

Support for the above considerations came from the ^{1}H-NMR chemical shift analysis. In the case of the *syn* isomer, which is intramolecularly hydrogen-bonded, the hydroxy proton resonance was strongly downfield (δ = 4.5 versus 2.4−2.7 for the *anti* isomer).[22] On the other hand, the characteristic H_a proton (Figure 2) of the *anti* isomer **3a** absorbs at lower field than that of the *syn* isomer **2a**, as reported for similar epoxy alcohols.[23] Moreover, for the *syn* isomer, the two geminal protons of the oxazoline ring have a chemical shift difference in Hertz ($\Delta\nu$) much larger than the coupling constant ($\Delta\nu/J > 10$, AX system); the *anti* isomer showed two doublets with a $\Delta\nu/J < 10$ (AB system). This probably could be due to the anisotropy of the methyl group on the same side of the two methylene protons that creates different magnetic environments (Figure 2). The steric compression of the methyl group in **3a** compared to that in **2a** is well reflected in the ^{13}C-NMR spectrum: The Me group signal in **3a** appears at higher field (δ = 18.27) with respect to that in **2a** (δ = 19.71).[24]

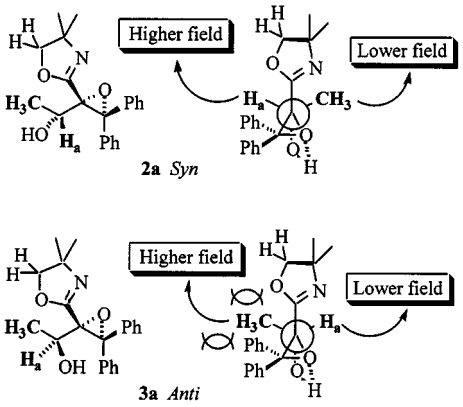
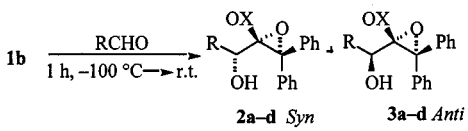


Figure 2. ^{1}H-NMR chemical shift analysis of *syn* and *anti* diastereomers **2a** and **3a**

Comparable results were obtained when **1b** was treated with other aldehydes. Indeed, the reaction with isobutyraldehyde, benzaldehyde, and *p*-tolualdehyde gave the diastereomeric epoxy alcohols **2b** and **3b**, **2c** and **3c**, **2d** and **3d**, respectively (Table 2). All these compounds could be separated and characterized as in the case of **2a** and **3a**.

It was interesting to observe that the deprotonation of *trans*-1-(4,4-dimethyl-2-oxazolinyl)-2-*p*-tolylepoxyethane (**1h**)[17] (Scheme 2) with *s*BuLi/TMEDA gave the oxiranyllithium **1i** which was configurationally stable for at least 1 h at −100°C. At present we cannot exclude that, under equilibrating conditions, the *trans* anion is much more

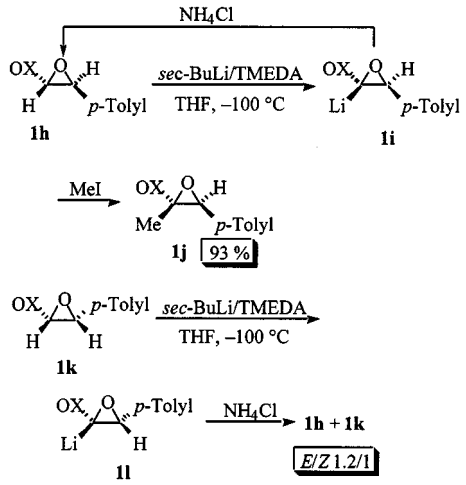
Table 2. Reaction of **1b** with aldehydes



R	Compound	Conversion (%)	Overall yield (%)[a]	dr[b] *syn*/*anti*
CH_3	**2a**/**3a**	> 95	68	1.3:1
$(CH_3)_2CH$	**2b**/**3b**	83	65	1.2:1
C_6H_5	**2c**/**3c**	> 95	83	1:1
p-Tolyl	**2d**/**3d**	83	70	1.8:1

[a] Based on converted material. − [b] Diastereomeric ratio, determined by weighing the isolated *syn* and *anti* diastereomers after column chromatography.

stable than the *cis* one. Starting *trans*-epoxide **1h** was quantitavely recovered upon quenching of **1i** with NH_4Cl and the reaction with MeI gave the (*E*)-oxirane **1j**[25a,25b] (93% yield). In contrast, lithiated intermediate **1l** from the *cis* isomer **1k** furnished a mixture of the isomers **1h** and **1k** upon acidic quenching in a 1.2:1 ratio (Scheme 2). This clearly indicates that the lithiated intermediate generated from **1k** is configurationally unstable. Such a different configurational stability has been reported for other oxiranyl anions.[1,26a,26b]

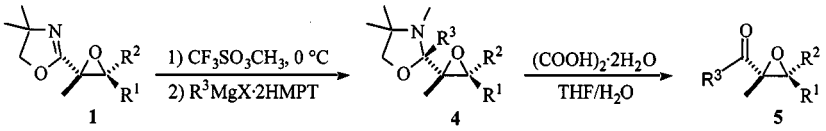


Scheme 2. Deprotonation of oxazolinyloxiranes **1h** and **1k** and reactions with electrophiles

The oxazolinyloxiranes above appear particularly useful as they can be deblocked to formyl- and acyloxiranes (Table 3). Indeed, treatment of oxiranyl epoxide **1d** first with CF_3SO_3Me and then with PhMgBr · 2 HMPT afforded oxiranyloxazolidines **4a** (inseparable mixture of diastereomers) that could be elaborated in the oxazolidine moiety to furnish benzoyloxirane **5a**. Similarly, methylation of **1d** with CF_3SO_3Me followed by the addition of MeMgBr · 2 HMPT gave oxazolidines **4b** (isolated isomers) which were subsequently deblocked to acetyloxirane **5b**. In the reaction of **1d** with cyclohexylMgCl · 2 HMPT, this Grignard reagent, for steric reasons, did not add to the preliminary activated

imine π-system with CF_3SO_3Me, but transferred a hydride ion to give oxazolidine **4c** (substantially one diastereomer) which was converted into formyloxirane **5c** upon hydrolysis with aqueous oxalic acid. The methylation−addition−deblocking sequence applied to oxiranyloxazolines **1j** and **1m** afforded acetyloxiranes **5d** and **5e**, respectively, going through oxazolidines **4d** (inseparable mixture of diastereomers) and **4e** (substantially one diastereomer). In both cases, the stereochemistry at the oxirane moiety was perfectly preserved (Table 3).

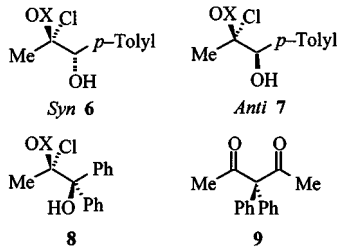
Table 3. Deblocking of oxazolinyloxiranes **1d**, **1j**, and **1m** to formyl- and acyloxiranes **5a−e**



				Overall yield (%)[a]			Yield (%)
		4a	$R^1 = R^2 = R^3 = Ph$	77 (d.r.1.5:1)[b,c]	**5a**	$R^1 = R^2 = R^3 = Ph$	69[d]
1d	$R^1 = R^2 = Ph$	**4b**	$R^1 = R^2 = Ph$; $R^3 = Me$	95 (d.r. 4:1)[b,e]	**5b**	$R^1 = R^2 = Ph$; $R^3 = Me$	77[f]
1j	$R^1 = p$-Tolyl; $R^2 = H$	**4c**	$R^1 = R^2 = Ph$; $R^3 = H$	51 (d.r. ≥ 95:5)[b,g]	**5c**	$R^1 = R^2 = Ph$; $R^3 = H$	77[a]
1m	$R^1 = H$; $R^2 = p$-Tolyl	**4d**	$R^1 = p$-Tolyl; $R^2 = H$; $R^3 = Me$	95 (d.r. 4:1)[b,c]	**5d**	$R^1 = p$-Tolyl; $R^2 = H$; $R^3 = Me$	40[h]
		4e	$R^1 = H$; $R^2 = p$-Tolyl; $R^3 = Me$	78 (d.r. ≥ 95:5)[b,g]	**5e**	$R^1 = H$; $R^2 = p$-Tolyl; $R^3 = Me$	40[h]

[a] Yield of isolated material. − [b] Diastereomeric ratio, determined by ^{1}H-NMR analysis on the crude reaction mixture; error ± 5% of the stated values. − [c] Inseparable mixture of diastereomers. − [d] Based on 33% conversion. − [e] Isolated diastereomeric oxazolidines; see Experimental Section. − [f] Yield determined by ^{1}H-NMR analysis on the crude reaction mixture.[26] − [g] Only one diastereomer was detected by ^{1}H NMR. − [h] Based on 50% conversion.

Finally it is worth noting that the (*E*)-oxiranyloxazoline **1j**, as well as **1d**, could also be synthesized in a single-step sequence from the intermediate chlorohydrins (*syn*-**6** and **8**, see Experimental Section) obtained in the reaction of 2-(1-chloroethyl)-4,4-dimethyl-2-oxazoline[30] with LDA and *p*-tolualdehyde or benzophenone, respectively, following a procedure reported for similar systems.[17]



Scheme 3. Chlorohydrins *syn*-**6**, *anti*-**7**, **8** and 3,3-diphenylpentane-2,4-dione **9**

In conclusion, in this paper we have shown how variously substituted oxazolinyloxiranes can be efficiently prepared upon deprotonation of their simpler parent epoxides and the resulting oxazolinyloxiranes can be deblocked to acyloxiranes. More work is in progress to apply this methodology to an asymmetric synthesis of acyl epoxides.[27]

Experimental Section

General: Tetrahydrofuran (THF) and diethyl ether (Et_2O) were freshly distilled under nitrogen from sodium benzophenone ketyl. TMEDA and diisopropylamine were distilled from finely powdered calcium hydride. Petroleum ether refers to the 40−60°C boiling fraction. Commercial solutions of *n*BuLi (as a solution in hexanes), *s*BuLi (cyclohexane/hexane, 92:8 solution), CH_3MgBr (3.0 M solution in Et_2O), PhMgBr (3.0 M solution in Et_2O), and (cyclohexyl)MgCl (2.0 M solution in Et_2O) from Aldrich were titrated by using *N*-pivaloyl-*o*-toluidine prior to use.[28] All other chemicals were of commercial grade (Aldrich) and distilled just prior to use. 2-Chloromethyl-4,4-dimethyl-2-oxazoline[29] and 2-(1-chloroethyl)-4,4-dimethyl-2-oxazoline[30] were prepared as reported. − NMR: Varian EM 390, Varian XL-200 (200 MHz and 50.3 MHz, for ^{1}H and ^{13}C, respectively), Bruker (300 MHz for ^{1}H). For ^{1}H NMR, $CDCl_3$ as solvent, δ_H = 7.24, TMS as internal standard; for ^{13}C NMR, $CDCl_3$ δ_C = 77.0, [D_6]acetone δ_C = 20.83. − IR: Perkin Elmer 283. − FTIR: Perkin Elmer 1600. − GC-MS spectrometry analyses were performed with a gas cromatograph HP 5995C (dimethylsilicon capillary column, 30 m, 0.25 mm i.d.) equipped with a mass-selective detector operating at 70 eV (EI). − Microanalyses were performed with a Carlo Erba Mod. 1106 C, H, N analyzer. Melting points are uncorrected. TLC was performed on Merck silica gel plates with F-254 indicator; visualization was accomplished by UV light (254 nm). Column chromatography was performed by using silica gel (70−230 mesh) with petroleum ether/diethyl ether (or AcOEt) mixtures as the eluent. A −100°C bath refers to a mixture of liquid nitrogen and methanol; the temperature was controlled with a spirit-filled low-temperature thermometer (Aldrich) and kept at a fixed value by adding liquid nitrogen from time to time. All reactions involving air-sensitive reagents were performed under nitrogen in oven-dried glassware using syringe-septum cap techniques. All products, of course, were racemates.

Preparation of Oxiranyloxazolines 1a, 1h, and 1k: These oxazolines were prepared according to the procedure reported in ref.[17] and showed the following data:

1-(4,4-Dimethyl-2-oxazolin-2-yl)-1,2-epoxy-2,2-diphenylethane (1a): Yellow oil. − ^{1}H NMR (200 MHz): δ = 0.92 (s, 3 H), 1.13 (s, 3 H), 3.59 (d, *J* = 8.0 Hz, 1 H), 3.75 (d, *J* = 8.0 Hz, 1 H), 4.02 (s, 1 H), 7.23-7.35 (m, 6 H), 7.43−7.48 (m, 4 H). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 27.63, 27.95, 59.24, 66.30, 67.20, 79.22, 126.72, 127.86, 127.99, 128.00, 128.22, 128.30, 135.63, 138.77, 159.86. − GC-MS (70 eV); *m/z* (%): 293 (58) [M^+], 264 (119), 238 (145), 208 (1000), 182 (109), 166 (163), 165 (823), 105 (199), 77 (211). − FTIR (film): $\tilde{\nu}$ = 3048 cm^{-1}, 2954, 1672 (C=N), 1654, 1443, 1255, 984, 755, 696.

(*E*)-1-(4,4-Dimethyl-2-oxazolin-2-yl)-1,2-epoxy-2-*p*-tolylethane (1h): Oil. − ^{1}H NMR (90 MHz): δ = 1.32 (s, 3 H), 1.35 (s, 3 H), 2.37

(s, 3 H), 3.61 (d, J = 1.5 Hz, 1 H), 4.04 (s, 2 H), 4.13 (d, J = 1.5 Hz, 1 H), 7.23 (s, 4 H). − GC-MS (70 eV); *m/z* (%): 231 (28) [M^+], 216 (89), 176 (149), 146 (1000), 119 (163), 91 (191), 77 (112). − IR (film): $\tilde{\nu}$ = 2960 cm^{-1}, 1655 (C=N), 1455, 1358, 1285, 985, 810.

(*Z*)-1-(4,4-Dimethyl-2-oxazolin-2-yl)-1,2-epoxy-2-*p*-tolylethane (1k): Oil. − ^{1}H NMR (90 MHz): δ = 1.04 (s, 3 H), 1.15 (s, 3 H), 2.34 (s, 3 H), 3.74 (s, 2 H), 3.83 (d, J = 5.2 Hz, 1 H), 4.20 (d, J = 5.2 Hz, 1 H), 7.07−7.37 (m, 4 H). − GC-MS (70 eV); *m/z* (%): 231 (25) [M^+], 216 (85), 176 (138), 146 (1000), 119 (155), 91 (191), 77 (122). − IR (film): $\tilde{\nu}$ = 2960 cm^{-1}, 1670 (C=N), 1510, 1455, 1245, 975, 800.

Preparation of Oxazolinyl Epoxides 1j and 1m: These epoxides were prepared as described in ref.[17] from 2-(1-chloroethyl)-4,4-dimethyl-2-oxazoline.[30] − A mixture of diastereomeric chlorohydrins *syn*-**6** and *anti*-**7** (Scheme 3) (1.3:1 *syn*/*anti* ratio,[25c] 71% overall yield) was obtained when 2-(1-chloroethyl)-4,4-dimethyl-2-oxazoline (1 mmol) was treated with LDA (1.2 mmol) and then with *p*-tolualdehyde (1.2 mmol). Chlorohydrins **6** and **7** could be separated by column chromatography (silica gel, hexane/AcOEt, 6:4) and converted quantitatively to (*E*)- and (*Z*)-[25a,25b]oxazolinyl epoxides **1j** and **1m**, respectively. The chlorohydrins and the epoxides showed the following data:

***syn*-2-Chloro-2-(4,4-dimethyl-2-oxazolin-2-yl)-1-*p*-tolyl-1-propanol (6):** M.p. 104−106°C (hexane/AcOEt). − ^{1}H NMR (200 MHz): δ = 1.31 (s, 3 H), 1.33 (s, 3 H), 1.62 (s, 3 H), 2.34 (s, 3 H), 4.04 (s, 2 H), 4.93 (br s, 1 H, exchanges with D_2O), 5.14 (s, 1 H), 7.12−7.16 (m, 2 H), 7.34−7.38 (m, 2 H). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.18, 22.00, 27.85, 28.06, 66.00, 67.50, 78.14, 79.40, 128.26, 128.63, 134.32, 137.87, 166.28. − GC-MS (70 eV); *m/z* (%): 246 (522) [M^+ − Cl], 228 (242), 161 (1000), 146 (420), 120 (402), 119 (562), 91 (718), 65 (215), 55 (229), 42 (218), 41 (232). − IR (KBr): $\tilde{\nu}$ = 3300−3100 cm^{-1} (O−H), 1655 (C=N), 1440, 1275, 1065, 805. − $C_{15}H_{20}ClNO_2$ (281.78): calcd. C 63.94, H 7.15, N 4.97; found C 64.05, H 7.31, N 5.23.

***anti*-2-Chloro-2-(4,4-dimethyl-2-oxazolin-2-yl)-1-*p*-tolyl-1-propanol (7):** M.p. 117−119°C (hexane/AcOEt). − ^{1}H NMR (200 MHz): δ = 1.23 (s, 3 H), 1.29 (s, 3 H), 1.59 (s, 3 H), 2.32 (s, 3 H), 4.03 (s, 2 H), 4.62 (br. s, 1 H, exchanges with D_2O), 5.08 (s, 1 H), 7.10−7.14 (m, 2 H), 7.29-7.33 (m, 2 H). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.20, 23.55, 27.83, 28.04, 67.46, 68.70, 77.67, 79.42, 128.24, 128.44, 134.12, 138.12, 165.63. − GC-MS (70 eV); *m/z* (%): 161 (38) [M^+ − *p*-C_6H_4CHO], 148 (222), 146 (730), 120 (756), 119 (852), 96 (761), 91 (1000), 65 (340), 63 (283). − IR (KBr): $\tilde{\nu}$ = 3300−3100 cm^{-1} (O−H), 1640 (C=N), 1450, 1068. − $C_{15}H_{20}ClNO_2$ (281.78): calcd. C 63.94, H 7.15, N 4.97; found C 64.34, H 7.44, N 5.01.

(*E*)-2-(4,4-Dimethyl-2-oxazolin-2-yl)-1,2-epoxy-1-*p*-tolylpropane (1j): Yellow oil. − ^{1}H NMR (300 MHz): δ = 1.30 (s, 6 H), 1.33 (s, 3 H), 2.32 (s, 3 H), 4.00 (s, 2 H), 4.36 (s, 1 H), 7.12−7.21 (m, 4 H). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 13.80 (q, ^1J_q = 128.9 Hz, CH_3C−O), 21.17 (mainly q with fine structure, ^1J_q = 126.8 Hz, CH_3−Ar), 28.26 (2 × CH_3C−N), 57.47, 62.33 (mainly d with fine structure, ^1J_d = 176.3 Hz, CH−O), 65.15, 79.54 (mainly t with fine structure, ^1J_t = 149.5 Hz, CH_2−O), 126.59, 128.86, 131.22, 137.82, 164.32. − GC-MS (70 eV); *m/z* (%): 245 (7) [M^+], 146 (999), 119 (137), 91 (155), 43 (228). − FTIR (film): $\tilde{\nu}$ = 2967 cm^{-1}, 1656 (C=N), 1461, 1133, 1078, 967, 811.

(*Z*)-2-(4,4-Dimethyl-2-oxazolin-2-yl)-1,2-epoxy-1-*p*-tolylpropane (1m): Yellow oil. − ^{1}H NMR (300 MHz): δ = 0.94 (s, 3 H), 1.01 (s, 3 H), 1.64 (s, 3 H), 2.25 (s, 3 H), 3.62 (s, 2 H), 3.91 (s, 1 H), 7.01−7.20 (2 m, 4 H). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 20.54 (qd, ^1J_q = 128.8, ^3J_d = 1.8 Hz, CH_3C−O), 21.16 (like qt, ^1J_q = 126.4, ^3J_t = 4.4 Hz, CH_3−Ar), 27.94 (CH_3C−N), 27.99 (CH_3C−N), 59.54 , 64.00 (mainly d with fine structure, ^1J_d = 175.5 Hz, CH−O), 67.31, 79.14 (mainly t with fine structure, ^1J_t = 149.4 Hz, CH_2−O), 126.47, 128.37, 131.07, 137.63, 161.75 (C=N). − GC-MS (70 eV); *m/z* (%): 245 (9) [M^+], 146 (1000), 91 (118), 43 (177). − FTIR (film): $\tilde{\nu}$ = 2968 cm^{-1}, 1674, (C=N), 1458, 1365, 1119, 1080, 808.

General Procedure for the Lithiation of the Epoxyoxazolines 1a, 1h, 1k, and Reaction with Electrophiles: The deprotonation of **1a** and the reaction with MeI are described as an example. To a solution of **1a** (200 mg, 0.68 mmol) and TMEDA (0.82 mmol, 0.12 mL) in 10 mL of dry Et_2O, under N_2 at −100°C, 1.26 M *s*BuLi (0.82 mmol, 0.65 mL) was added dropwise. The resulting yellow solution of the putative oxiranyl anion was stirred at −100°C for 2 h. MeI (0.89 mmol) in 3 mL of Et_2O was then added slowly. Stirring at −100°C was continued for 1 h. Then the reaction mixture was allowed to warm to room temp., quenched with sat. aq. NH_4Cl and extracted with Et_2O (3 × 10 mL). The combined organic layers were dried with Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography (silica gel; petroleum ether/Et_2O, 1:1) to give **1d** (190 mg, 62% yield). The same eluent was also used to purify **1c**, **1e**, and **1f**. In the case of **1g** and for diastereomeric epoxy alcohols **2a**/**3a**, **2b**/**3b**, **2c**/**3c**, **2d**/**3d** a 7:3 petroleum ether/AcOEt mixture as the eluent was used. − **1d** could also be prepared more conveniently through the reaction of 2-(1-chloroethyl)-4,4-dimethyl-2-oxazoline[30] with benzophenone in the presence of LDA likewise as described in ref.[17] The chlorohydrin **8** was purified by column chromatography (silica gel, petroleum ether/Et_2O, 7:3) (64% yield) and subsequently cyclized quantitatively to **1d** in NaOH/*i*PrOH.[25b] − The new compounds showed the following data:

1-(4,4-Dimethyl-2-oxazolin-2-yl)-1,2-epoxy-1-trimethylsilyl-2,2-diphenylethane (1c): M.p. 107−109°C (isooctane). − ^{1}H NMR (200 MHz): δ = −0.11 (s, 9 H), 0.76 (s, 3 H), 0.96 (s, 3 H), 3.59 and 3.62 (2× d, AB system, J = 8.0 Hz, 2 H), 7.17−7.30 (m, 6 H), 7.52−7.59 (m, 4 H). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = −2.59, 27.67, 27.97, 62.02, 66.96, 70.62, 78.90, 126.90, 127.25, 127.53, 127.56, 127.60, 127.78, 128.00, 139.32, 139.42, 162.89. − GC-MS (70 eV); *m/z* (%): 365 (159) [M^+], 364 (519), 350 (149), 294 (112), 280 (411), 176 (168), 166 (140), 165 (403), 77 (107), 73 (1000). − FTIR (KBr): $\tilde{\nu}$ = 3061 cm^{-1}, 2963, 1644 (C=N), 1358 , 1293, 1244, 845, 704, 623. − $C_{22}H_{27}NO_2Si$ (365.55): calcd. C 72.29 H 7.44, N 3.83; found C 72.60, H 7.74, N 3.63.

2-(4,4-Dimethyl-2-oxazolin-2-yl)-1,2-epoxy-1,1-diphenylpropane (1d): M.p. 103−104°C (hexane). − ^{1}H NMR (300 MHz): δ = 0.87 (s, 3 H), 1.07 (s, 3 H), 1.43 (s, 3 H), 3.54 (d, J = 8.0 Hz, 1 H), 3.69 (d, J = 8.0 Hz, 1 H), 7.18−7.34 (m, 6 H), 7.47−7.51 (m, 4 H). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 17.63, 27.72, 27.88, 62.92, 67.29, 70.48, 79.24 (CH_2−O), 127.14, 125.49, 127.68, 127.81, 128.26, 137.92, 138.49, 163.03 (C=N). − GC-MS (70 eV); *m/z* (%): 307 (13) [M^+], 208 (1000), 165 (666), 105 (130), 77 (193), 43 (271). − FTIR (KBr): $\tilde{\nu}$ = 3044 cm^{-1}, 2966, 1666 (C=N), 1444, 1294, 1100, 966, 700. − $C_{20}H_{21}NO_2$ (307.39): calcd. C 78.15, H 6.89, N 4.56; found C 78.16, H 6.86, N 4.56.

4-(4,4-Dimethyl-2-oxazolin-2-yl)-4,5-epoxy-5,5-diphenyl-1-pentene (1e): Oil. − ^{1}H NMR (300 MHz): δ = 0.87 (s, 3 H), 1.05 (s, 3 H), 1.94 (ddt, J = 14.8, 5.7, 1.5 Hz, 1 H), 2.85 (ddt, J = 14.8, 7.9, 1.0 Hz, 1 H), 3.53 and 3.69 (2 × d, AB system, J = 8.0 Hz, 2 H), 5.05−5.16 (3 m, 2 H), 5.75−5.93 (m, 1 H), 7.15−7.37 (m, 6 H), 7.48−7.54 (m, 4 H). − ^{13}C NMR (APT, 50.3 MHz, $CDCl_3$): δ = 27.62 (CH_3), 27.84 (CH_3), 35.98 (CH_2−C=), 65.65, 67.28, 70.39,

76.37 (CH_2−O), 118.36 (CH_2=), 127.10, 127.13, 127.53, 127.77, 128.30, 131.83 (*C*H=), 137.64, 138.22, 161.54 (*C*=N). − GC-MS (70 eV); *m/z* (%): 333 (5) [M^+], 332 (3), 208 (1000), 165 (558), 105 (135), 77 (191), 41 (271). − FTIR (film): $\tilde{\nu}$ = 3055 cm^{-1} (OH), 1664 (C=N), 1488, 1444, 1361, 1300, 966, 916, 750, 700, 627.

3-(4,4-Dimethyl-2-oxazolin-2-yl)-3,4-epoxy-2-methyl-4,4-diphenyl-2-butanol (1f): M.p. 117−119°C (isooctane). − ^{1}H NMR (200 MHz): δ = 0.85 (s, 3 H), 0.94 (s, 3 H), 1.13 (s, 3 H), 1.41 (s, 3 H), 2.55 (br. s, 1 H, exchanges with D_2O), 3.51 and 3.63 (2 × d, AB system, *J* = 8.0 Hz, 2 H), 7.15−7.35 (m, 6 H), 7.52−7.62 (2 m, 4 H). − ^{13}C NMR (APT, 50.3 MHz, $CDCl_3$): δ = 26.96 (CH_3), 27.03 (CH_3), 27.47 (CH_3), 27.54 (*C*H_3), 67.22, 70.90, 71.26, 78.90 (CH_2−O), 126.56, 126.76, 127.41, 127.71, 127.81, 128.37, 138.33, 139.42, 161.42 (*C*=N). − GC-MS (70 eV); *m/z* (%): 351 (2) [M^+], 336 (1000), 294 (74), 292 (108), 208 (602), 165 (627), 105 (187), 77 (157), 59 (464). − FTIR (KBr): $\tilde{\nu}$ = 3500−3200 cm^{-1} (OH), 3061, 1667 (C=N), 1528, 1450, 1361, 1178, 1028, 961, 906, 739. − $C_{22}H_{25}NO_3$ (351.44): calcd. C 75.19, H 7.17, N 3.98; found C 75.15, H 7.33, N 3.58.

1-(4,4-Dimethyl-2-oxazolin-2-yl)-1,2-epoxy-1-(1-hydroxy-1-cyclohexyl)-2,2-diphenylethane (1g): Paste. − ^{1}H NMR (200 MHz): δ = 0.85 (s, 3 H), 0.91 (s, 3 H), 1.16−1.55 (m, 8 H), 1.73−1.91 (m, 2 H), 2.1 (br. s, 1 H, exchanges with D_2O), 3.49 and 3.61 (2 × d, AB system, *J* = 8.0 Hz, 2 H), 7.13−7.33 (m, 6 H), 7.50−7.61 (2 m, 4 H). − ^{13}C NMR (APT, 50.3 MHz, $CDCl_3$): δ = 21.10 (CH_2), 21.29 (CH_2), 25.44 (CH_2), 27.50 (CH_3), 27.52 (CH_3), 33.71 (CH_2), 34.26 (CH_2), 67.19, 70.93, 71.26, 72.30, 78.73 (CH_2−O), 126.58, 126.67, 127.31, 127.59, 127.75, 128.33, 138.65, 139.57, 161.25 (*C*=N). − GC-MS (70 eV); *m/z* (%): 391 (88) [M^+], 390 (231), 348 (156), 292 (175), 244 (255), 209 (386), 208 (591), 165 (728), 99 (1000), 81 (493), 55 (314), 41 (265). − FTIR (KBr): $\tilde{\nu}$ = 3600−3200 cm^{-1} (OH), 1640 (C=N), 1440, 1360, 1260, 742, 700.

***syn*-3-(4,4-Dimethyl-2-oxazolin-2-yl)-3,4-epoxy-4,4-diphenyl-2-butanol (2a):** M.p. 112−114°C (hexane). − ^{1}H NMR (200 MHz): δ = 1.08 (s, 3 H), 1.14 (s, 3 H), 1.28 (d, *J* = 6.5 Hz, 3 H), 3.28 (d, *J* = 8.2 Hz, 1 H), 3.27−3.37 (m overlap d at δ = 3.28, C*H*−O oxazoline ring; q centered at δ = 3.32 after exchange with D_2O), 3.74 (d, *J* = 8.2 Hz, 1 H), 4.58 (br. d, *J* = 9.9 Hz, 1 H, exchanges with D_2O), 7.20−7.37 (m, 6 H), 7.44−7.62 (2 m, 4 H). − ^{13}C NMR (APT, 50.3 MHz, $CDCl_3$): δ = 19.71 (CH_3−CHOH), 27.80 (CH_3), 28.04 (CH_3), 66.70, 67.34 (*C*H−OH), 67.81, 72.12, 78.52 (CH_2−O), 126.77, 127.19, 127.71, 127.92, 128.02, 128.39, 137.05, 138.18, 161.55 (*C*=N). − GC-MS (70 eV); *m/z* (%): 337 (17) [M^+], 322 (90), 292 (63), 208 (1000), 165 (571), 105 (173), 77 (164), 45 (157). − FTIR (KBr): $\tilde{\nu}$ = 3367 cm^{-1} (OH), 2978, 1644 (C=N), 1444, 1367, 1078, 700. − $C_{21}H_{23}NO_3$ (337.42): calcd. C 74.75, H 6.87, N 4.15; found C 75.15, H 7.19, N 3.98.

***anti*-3-(4,4-Dimethyl-2-oxazolin-2-yl)-3,4-epoxy-4,4-diphenyl-2-butanol (3a):** White solid, m.p. 183−185°C (isooctane). − ^{1}H NMR (200 MHz: δ = 0.89 (s, 3 H), 1.03 (s, 3 H), 1.33 (d, *J* = 6.6 Hz), 2.4−2.7 (br. s, 1 H, exchanges with D_2O), 3.58 (q partially overlap AB system CH_2−O), 3.66 and 3.69 (2 × d, AB system CH_2−O, *J* = 8.0 Hz, 2 H), 7.20−7.37 (m, 6 H), 7.48−7.55 (m, 4 H). − ^{13}C NMR (APT, 50.3 MHz, $CDCl_3$): δ = 18.27 (CH_3−CHOH), 27.68 (CH_3), 27.77 (*C*H_3), 67.23, 69.08 (*C*H−OH), 69.21, 71.13, 78.91 (CH_2−O), 126.91, 127.03, 127.68, 127.71, 127.87, 127.98, 128.39, 137.14, 138.11, 159.79 (*C*=N). − GC-MS (70 eV); *m/z* (%): 337 (14) [M^+], 322 (145), 292 (56), 208 (999), 165 (486), 105 (125), 77 (101), 45 (65). − FTIR (KBr): $\tilde{\nu}$ = 3236 cm^{-1} (OH), 2967, 1678 (C=N), 1444, 1294, 1128, 1106, 744, 700. − $C_{21}H_{23}NO_3$ (337.42): calcd. C 74.75, H 6.87, N 4.15; found C 74.72, H 7.14, N 3.94.

***syn*-2-(4,4-Dimethyl-2-oxazolin-2-yl)-1,2-epoxy-4-methyl-1,1-diphenyl-3-pentanol (2b):** Oil. − ^{1}H NMR (200 MHz): δ = 0.94 and 0.96 (2 × d, *J* = 6.6 Hz, 6 H), 1.05 (s, 3 H), 1.08 (s, 3 H), 1.73−1.90 (m, 1 H), 2.74 (d, *J* = 8.7 Hz, 1 H), 3.27 (d, *J* = 8.2 Hz, 1 H), 3.73 (d, *J* = 8.2 Hz, 1 H), 4.1−4.3 (br. s, 1 H, exchanges with D_2O), 7.20−7.37 (2 m, 6 H), 7.49−7.64 (2 m, 4 H). − ^{13}C NMR (APT, 50.3 MHz, $CDCl_3$): δ = 18.54 (CH_3−CH), 19.27 (CH_3−CH), 27.75 (CH_3), 27.84 (CH_3), 33.37 (*C*H−CHOH), 66.12, 67.75, 69.76, 76.50 (*C*H−OH), 78.61 (CH_2−O), 127.02, 127.27, 127.67, 127.90, 128.34, 137.13, 138.26, 161.91 (*C*=N). − GC-MS (70 eV); *m/z* (%): 365 (9) [M^+], 322 (252), 294 (65), 208 (1000), 165 (617), 105 (223), 77 (167), 55 (242), 43 (199), 41 (248). − FTIR (film): $\tilde{\nu}$ = 3404 cm^{-1} (OH), 3056, 1644 (C=N), 1461, 1394, 1083, 1044, 972, 750, 700, 622.

***anti*-2-(4,4-Dimethyl-2-oxazolin-2-yl)-1,2-epoxy-4-methyl-1,1-diphenyl-3-pentanol (3b):** White solid, m.p. 142−144°C (isooctane). − ^{1}H NMR (200 MHz): δ = 0.73 (s, 3 H), 0.89 and 0.92 (2 × d, *J* = 6.6 Hz, 6 H), 1.04 (s, 3 H), 1.80−1.90 (br. s, 1 H, exchanges with D_2O), 1.91−2.08 (m, 1 H), 3.42 (d, *J* = 7.3 Hz, 1 H), 3.65 (s, 2 H), 7.16−7.36 (m, 6 H), 7.51−7.58 (2 m, 4 H). − ^{13}C NMR (APT, 50.3 MHz, $CDCl_3$): δ = 17.92 (CH_3−CH), 19.84 (CH_3−CH), 27.45 (CH_3), 27.73 (*C*H_3), 31.27 (*C*H−CHOH), 67.01, 68.51, 71.17, 75.35 (*C*H−OH), 79.07 (CH_2−O), 127.12, 127.19, 127.68, 127.80, 127.97, 128.28, 137.30, 138.37, 160.01 (*C*=N). − GC-MS (70 eV); *m/z* (%): 365 (7) [M^+], 322 (358), 208 (1000), 180 (132), 165 (481), 105 (164), 77 (137), 55 (134), 43 (107), 41 (113). − FTIR (KBr): $\tilde{\nu}$ = 3605 cm^{-1} (sharp, OH free), 3250 (broad, OH bonded), 1661 (C=N), 1447, 1365, 1054, 977, 759, 704, 627. − $C_{23}H_{27}NO_3$ (365.47): calcd. C 75.59, H 7.45, N 3.83; found C 75.98, H 7.85, N 3.7.

***syn*-2-(4,4-Dimethyl-2-oxazolin-2-yl)-2,3-epoxy-1,3,3-triphenyl-1-propanol (2c):** M.p. 140−142°C (hexane). − ^{1}H NMR (300 MHz): δ = 0.90 (s, 3 H), 0.99 (s, 3 H), 3.08 (d, *J* = 8.1 Hz, 1 H), 3.45 (d, *J* = 8.1 Hz, 1 H), 4.34 (s, 1 H), 5.55 (br. s, 1 H, exchanges with D_2O), 7.18−7.31 (m, 7 H), 7.35−7.40 (m, 2 H), 7.44−7.46 (m, 2 H), 7.52−7.55 (m, 2 H), 7.72−7.78 (m, 2 H). − ^{13}C NMR (APT, 50.3 MHz, $CDCl_3$): δ = 27.56 (CH_3), 27.68 (*C*H_3), 66.93, 67.69, 71.33, 71.88 (*C*H−OH), 78.35 (CH_2−O), 125.72, 126.90, 127.21, 127.35, 127.84, 127.89, 127.93, 128.19, 128.49, 136.97, 137.93, 140.61, 161.58 (*C*=N). − GC-MS (70 eV); *m/z* (%): 399 (58) [M^+], 380 (123), 292 (373), 208 (1000), 165 (807), 107 (471), 105 (308), 79 (209), 77 (378). − FTIR (KBr): $\tilde{\nu}$ = 3432 cm^{-1} (OH), 3087, 2923, 1655 (C=N), 1450, 1383, 1044, 966, 700, 600. − $C_{26}H_{25}NO_3$ (399.49): calcd. C 78.17, H 6.31, N 3.51; found C 78.51, H 6.45, N 3.18.

***anti*-2-(4,4-Dimethyl-2-oxazolin-2-yl)-2,3-epoxy-1,3,3-triphenyl-1-propanol (3c):** White solid, m.p. 113−115°C (isooctane). − ^{1}H NMR (200 MHz): δ = 0.65 (s, 3 H), 0.83 (s, 3 H), 2.5−2.8 (br. s, 1 H, exchanges with D_2O), 3.30 and 3.40 (2 × d, AB system, *J* = 8.0 Hz, 2 H), 4.97 (s, 1 H), 7.17−7.41 (m, 11 H), 7.50−7.63 (2 × m, 4 H). − ^{13}C NMR (APT, 50.3 MHz, $CDCl_3$): δ = 27.18 (*C*H_3), 27.45 (*C*H_3), 66.91, 68.84, 70.78, 72.42 (*C*H−OH), 78.79 (*C*H_2−O), 126.96, 127.29, 127.66, 127.75, 127.87, 128.18, 128.60, 137.03, 137.99, 139.15, 159.91 (*C*=N). − GC-MS (70 eV); *m/z* (%): 399 (87) [M^+], 380 (140), 292 (340), 208 (1000), 165 (762), 107 (419), 105 (278), 79 (199), 77 (344). − FTIR (KBr): $\tilde{\nu}$ = 3233 cm^{-1} (broad, OH), 3056, 2967, 1661 (C=N), 1500, 1450, 1083, 967, 739, 700. − $C_{26}H_{25}NO_3$ (399.49): calcd. C 78.17, H 6.31, N 3.51; found C 78.57, H 6.71, N 3.26.

***syn*-2-(4,4-Dimethyl-2-oxazolin-2-yl)-2,3-epoxy-3,3-diphenyl-1-*p*-tolyl-1-propanol (2d):** M.p. 136−138°C (hexane). − ^{1}H NMR (200 MHz): δ = 0.94 (s, 3 H), 1.00 (s, 3 H), 2.29 (s, 3 H), 3.09 (d, *J* =

8.2 Hz, 1 H), 3.48 (d, *J* = 8.2 Hz, 1 H), 4.31 (s, 1 H), 7.07−7.43 (2 m, 11 H; 10 H after exchange with D_2O), 7.52−7.76 (2 m, 4 H). − ^{13}C NMR (APT, 50.3 MHz, $CDCl_3$): δ = 21.07 (*C*H_3−Ar), 27.60 (*C*H_3), 27.73 (*C*H_3), 66.98, 67.70, 71.39, 71.82 (*C*H−OH), 78.32 (*C*H_2−O), 125.64, 126.91, 127.24, 127.78, 127.91, 128.15, 128.47, 128.58, 136.88, 137.02, 137.54, 138.00, 161.63 (*C*=N). − GC-MS (70 eV); *m/z* (%): 413 (60) [M^+], 394 (106), 293 (283), 292 (473), 246 (99), 230 (118), 208 (417), 165 (794), 121 (1000), 105 (236), 93 (240), 91 (254), 77 (330). − FTIR (KBr): $\tilde{\nu}$ = 3407 cm^{-1} (OH), 3062, 1656 (C=N), 1449, 1390, 1048, 704, 625. − $C_{27}H_{27}NO_3$ (413.51): calcd. C 78.42, H 6.58, N 3.39; found C 78.25, H 6.83, N 3.24.

***anti*-2-(4,4-Dimethyl-2-oxazolin-2-yl)-2,3-epoxy-3,3-diphenyl-1-*p*-tolyl-1-propanol (3d):** White solid, m.p. 143−145°C (hexane). − ^{1}H NMR (200 MHz): δ = 0.66 (s, 3 H), 0.85 (s, 3 H), 2.29 (s, 3 H), 2.35−2.55 (br. s, 1 H, exchanges with D_2O), 3.34 and 3.42 (2 × d, AB system, *J* = 8.0 Hz, 2 H), 4.93 (s, 1 H), 7.04−7.41 (m, 10 H), 7.49−7.63 (2× m, 4 H). − ^{13}C NMR (APT, 50.3 MHz, $CDCl_3$): δ = 21.15 (*C*H_3−Ar), 27.22 (*C*H_3), 27.47 (*C*H_3), 66.94, 68.94, 70.85, 72.39 (*C*H−OH), 78.79 (*C*H_2−O) , 127.00, 127.19, 127.65, 127.75, 128.16, 128.56, 136.14, 137.12 137.56, 138.06, 159.91 (*C*=N). − GC-MS (70 eV); *m/z* (%): 413 (37) [M^+], 394 (74), 293 (394), 292 (637), 246 (187), 230 (236), 208 (612), 165 (887), 121 (999), 105 (190), 93 (211), 91 (225), 77 (245). − FTIR (KBr): $\tilde{\nu}$ = 3200 cm^{-1} (OH), 3057, 2967, 1656 (C=N), 1444, 1256, 1083, 1017, 806, 700. − $C_{27}H_{27}NO_3$ (413.51): calcd. C 78.42, H 6.58, N 3.39; found C 78.66, H 6.86, N 3.27.

General Procedure for the Synthesis of Oxazolidinyl Epoxides 4a−e: The preparation of **4a** is described as an example. To a solution of oxazolinyl epoxide **1d** (468 mg, 1.52 mmol) in dry THF (3.5 mL), under N_2 at 0°C, methyl triflate (2.29 mmol, 259 μL) was added directly. After 30 min, to the resulting *N*-methyloxazolinium salt a complex of PhMgBr (3.0 M, 0.55 mL) with hexamethylphosphorous triamide[31] (HMPT, 3.34 mmol, 607 μL) in THF (2.0 mL) was added dropwise at room temp. The reaction mixture was stirred for 50 min, then quenched with sat. aq. NH_4Cl and extracted with Et_2O (3 × 10 mL). The combined organic layers were dried with Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by flash chromatography (petroleum ether/Et_2O, 8:2) to give **4a** (468 mg, 77% overall yield) as an inseparable 1.5:1 mixture of diastereomers (checked by ^{1}H- and ^{13}C-NMR analyses). In the case of **4c**, **4d**, and **4e** a (8−9):(2−1) petroleum ether/Et_2O mixture was used as the eluent. The new oxazolidinyl epoxides showed the following data:

1,2-Epoxy-1,1-diphenyl-2-(3,4,4-trimethyl-2-phenyl-1,3-oxazolidin-2-yl)propane (4a): Waxy solid. − ^{1}H NMR (300 MHz): δ = 0.46 (s, 3 H, major), 0.79 (s, 3 H, major), 0.87 (s, 3 H, minor), 1.13 (s, 3 H, major), 1.17 (s, 3 H, minor), 1.18 (s, 3 H, minor), 1.20 (s, 3 H, minor), 2.05 (s, 3 H, major), 3.78 (d, *J* = 7.3 Hz, 1 H, major), 3.87 (d, *J* = 7.3 Hz, 1 H, major), 3.92 (d, *J* = 7.5 Hz, 1 H, minor), 4.23 (d, *J* = 7.5 Hz, 1 H, minor), 7.03−7.24 (m, 4 H major + 4 H minor), 7.30−7.41 (m, 6 H major + 6 H minor), 7.47−7.68 (m, 5 H major + 5 H minor). − ^{13}C NMR [50.3 MHz, $(CD_3)_2CO$], (major + minor): δ = 20.01, 20.57, 21.17, 22.42, 23.05, 24.14, 60.69, 62.23, 68.58, 70.99, 73.90, 74.29, 77.80, 78.20, 97.79, 100.75, 126.10, 126.65, 126.79, 127.10, 127.28, 127.38, 127.45, 127.83, 127.99, 128.09, 128.14, 128.50, 128.75, 128.79, 140.19, 140.49, 142.06, 142.24, 143.96, 144.43. − GC-MS (70 eV); *m/z* (%) (minor): 384 (1) [$M^+ - CH_3$], 190 (1000), 165 (105), 105 (179), 77 (117). − GC-MS (70 eV); *m/z* (%) (major): 384 (2) [$M^+ - CH_3$], 190 (1000), 165 (128), 105 (208), 77 (143). − FTIR (KBr) (major + minor): $\tilde{\nu}$ = 3088 cm^{-1}, 2944, 1600, 1577, 1488, 1444, 1377, 1355, 1261, 1166, 1066, 744 , 700.

1,2-Epoxy-1,1-diphenyl-2-(2,3,4,4-tetramethyl-1,3-oxazolidin-2-yl)-propane (4b): Diastereomeric oxazolidines (4:1 ratio, ^{1}H-NMR and ^{13}C-NMR analyses) could be isolated by chromatography on silica gel (petroleum ether/AcOEt, 9:1): 95% overall yield. − **Minor Diastereomer:** Oil. − ^{1}H NMR (300 MHz): δ = 0.88 (s, 3 H), 1.02 (s, 3 H), 1.13 (s, 3 H), 1.18 (s, 3 H), 1.91 (s, 3 H), 3.62 (d, *J* = 7.7 Hz, 1 H), 3.69 (d, *J* = 7.7 Hz, 1 H), 7.10−7.60 (3 m, 10 H). − ^{13}C NMR [50.3 MHz, $(CD_3)_2CO$]: δ = 18.57, 20.41, 21.72, 24.88, 27.19, 75.83, 77.33, 77.96, 78.95, 98.65, 126.88, 126.98, 127.26, 127.94, 128.20, 128.70, 142.05. − GC-MS (70 eV); *m/z* (%): 322 (7) [$M^+ - CH_3$], 165 (156), 128 (1000), 74 (108), 56 (208). − FTIR (film): $\tilde{\nu}$ = 2962 cm^{-1}, 1444, 1260, 1096, 1022, 799, 705. − **Major Diastereomer:** White solid, m.p. 93−95°C (hexane). − ^{1}H NMR (300 MHz): δ = 0.97 (s, 3 H), 1.04 (s, 3 H), 1.20 (s, 3 H), 1.37 (s, 3 H), 2.33 (s, 3 H), 3.28 (d, *J* = 7.5 Hz, 1 H), 3.76 (d, *J* = 7.5 Hz, 1 H), 7.22−7.53 (3 m, 10 H). − ^{13}C NMR [50.3 MHz, $(CD_3)_2CO$]: δ = 18.19, 21.13, 21.42, 24.24, 60.21, 68.30, 72.41, 74.56, 77.32, 96.01, 126.44, 126.87, 127.15, 127.24, 127.93, 128.68, 142.49, 143.94. − GC-MS (70 eV); *m/z* (%): 322 (7) [$M^+ - CH_3$], 165 (156), 128 (1000), 74 (108), 56 (208). − FTIR (film): $\tilde{\nu}$ = 2921 cm^{-1}, 1444, 1253, 1100, 1053, 1026, 703, 686. − $C_{22}H_{27}NO_2$ (337.46): calcd. C 78.30, H 8.06, N 4.15; found C 78.14, H 8.08, N 3.91.

1,2-Epoxy-1,1-diphenyl-2-(3,4,4-trimethyl-1,3-oxazolidin-2-yl)propane (4c): Diastereomeric ratio: ≥ 95:5 − White solid, m.p. 118−120°C (hexane), 51% overall yield. − ^{1}H NMR (200 MHz): δ = 0.81 (s, 3 H), 1.10 (s, 3 H), 1.16 (s, 3 H), 2.21 (s, 3 H), 3.49 (s, 1 H), 3.62 (s, 2 H), 7.16−7.35 (m, 6 H), 7.44−7.57 (m, 4 H). − ^{13}C NMR [50.3 MHz, $(CD_3)_2CO$]: δ = 12.94, 16.54, 23.29, 57.80, 59.99, 68.08, 69.27, 79.36, 95.62, 127.40, 127.70, 127.77, 128.01, 128.60, 128.75, 140.39, 141.34. − GC-MS (70 eV); *m/z* (%): 323 (6) [M^+], 165 (1063), 114 (10000), 60 (1125), 42 (1548). − FTIR (KBr): $\tilde{\nu}$ = 2971 cm^{-1}, 2865, 1495, 1447, 1069, 1018, 768 , 706. − $C_{21}H_{25}NO_2$ (323.43): calcd. C 77.98, H 7.79, N 4.33; found C 77.58, H 8.05, N 3.98.

(*E*)-1,2-Epoxy-2-(2,3,4,4-tetramethyl-1,3-oxazolidin-2-yl)-1-*p*-tolylpropane (4d): Inseparable mixture of diastereomers (4:1 ratio, ^{1}H- and ^{13}C-NMR analyses): oil, 95% overall yield. − ^{1}H NMR (90 MHz), selected data: δ = 0.85 (s, 3 H, major), 0.97 (s, 3 H, major), 1.13 (s, 3 H, major), 1.49 (s, 3 H, major), 2.19 (s, 3 H, major), 2.31 (s, 3 H, major), 3.43 and 3.75 (2 × d, AB system, *J* = 5.0 Hz, 2 H, minor), 3.46 and 3.74 (2 × d, AB system, *J* = 7.5 Hz, 2 H maior), 7.07−7.32 (m, 4 H minor + 4 H major). − GC-MS (70 eV); *m/z* (%) (minor): 260 (6) [$M^+ - CH_3$], 128 (1000), 86 (72), 74 (90), 56 (185). − GC-MS (70 eV); *m/z* (%) (minor): 260 (12) [$M^+ - CH_3$], 128 (999), 86 (78), 74 (95), 56 (207). − FTIR (film) (major + minor), selected data: $\tilde{\nu}$ = 2928 cm^{-1}, 1465, 1366, 1262, 1123, 1074, 750.

(*Z*)-1,2-Epoxy-2-(2,3,4,4-tetramethyl-1,3-oxazolidin-2-yl)-1-*p*-tolylpropane (4e): Diastereomeric ratio ≥ 95:5. − Oil, 78% . − ^{1}H NMR (90 MHz): δ = 1.10 (s, 3 H), 1.17 (s, 3 H), 1.18 (s, 3 H), 1.43 (s, 3 H), 2.36 (s, 3 H), 2.40 (s, 3 H), 3.71 (s, 2 H), 4.52 (s, 1 H), 7.22 (s, 4 H). − GC-MS (70 eV); *m/z* (%): 260 (2) [$M^+ - CH_3$], 128 (1000), 91 (46), 74 (114), 56 (228). − FTIR (film): $\tilde{\nu}$ = 2972 cm^{-1}, 1517, 1467, 1366, 1263, 1135, 1076, 1045, 803.

Deblocking of Oxazolidines 4a−e to Acyloxiranes 5a−e: Oxazolidines **4a−e** were deblocked to acyloxiranes **5a−e** according to the procedure reported in ref.[17] With the exception of **5b** (see below) all the other acyl epoxides were purified by column chromatography [silica gel, petroleum ether/Et_2O, (7−9):(3−1)]. The acyl epoxides had the following data (see also Table 3):

2,3-Epoxy-2-methyl-1,3,3-triphenylpropan-1-one (5a): Oil, 69% [16 h, room temp., 1.8 equiv. $(COOH)_2 \cdot 2\ H_2O$]. – ^{1}H NMR (300 MHz): δ = 1.54 (s, 3 H), 7.05–7.10 (m, 3 H), 7.27–7.58 (m, 10 H), 7.83–7.85 (m, 2 H). – GC-MS (70 eV); *m/z* (%): 314 (187) [M^+], 272 (153), 271 (225), 209 (69), 165 (1000), 105 (427), 77 (502), 51 (191), 43 (89). – FTIR (film): $\tilde{\nu}$ = 3060 cm^{-1}, 2927, 1681(C=O), 1448, 1278, 1165,1073, 1090, 703.

3,4-Epoxy-3-methyl-4,4-diphenylbutan-2-one (5b): A mixture of the expected epoxy ketone **5b**[32] (77%) and 3,3-diphenylpentane-2,4-dione (**9**) (23%) (Scheme 3) (^{1}H NMR and MS inspection) was obtained when the oxazolidine **4b** (diastereomers, 0.28 mmol) was treated with an aq. $(COOH)_2 \cdot 2\ H_2O$ solution (10 mL of 3.2% w/w; temp. 60–65°C; 3 d). Attempted separation by silica gel chromatography of **5b** and **9** failed as **5b** isomerized quantitatively to **9**. Such an isomerization occurs frequently with β,β-diphenyl epoxy ketones.[33] To our knowledge, **5b** had been isolated in pure form only by preparative gas-cromatographic analysis.[32]

2,3-Epoxy-2-methyl-3,3-diphenylpropanal (5c): Oil, 77% [32 h, room temp., 1.0 equiv. of $(COOH)_2 \cdot 2\ H_2O$]. – ^{1}H NMR (90 MHz): δ = 1.30 (s, 3 H), 7.11–7.59 (m, 10 H), 8.98 (s, 1 H). – GC-MS (70 eV); *m/z* (%): 238 (2) [M^+], 237 (8), 195 (552), 165 (1000), 105 (117), 77 (266), 51 (185), 43 (257). – FTIR (film): $\tilde{\nu}$ = 3055 cm^{-1}, 2933, 2833, 1722 (C=O), 1494, 1450, 1072, 1016, 766, 750, 700.

(*E*)-3,4-Epoxy-3-methyl-4-*p*-tolylbutan-2-one (5d): Oil , 40% [2 d, room temp., 11 equiv. of $(COOH)_2 \cdot 2\ H_2O$]. – ^{1}H NMR (300 MHz): δ = 1.62 (s, 3 H), 1.80 (s, 3 H), 2.30 (s, 3 H), 4.04 (s, 1 H), 7.08–7.38 (m, 4 H). – GC-MS (70 eV); *m/z* (%): 190 (686) [M^+], 147 (494), 119 (561), 105 (378), 104 (530), 103 (558), 91 (419), 78 (636), 43 (999). – FTIR (film): $\tilde{\nu}$ = 1716 cm^{-1} (C=O).

(*Z*)-3,4-Epoxy-3-methyl-4-*p*-tolylbutan-2-one (5e): Oil, 40% [2 d, room temp., 8 equiv. of $(COOH)_2 \cdot 2\ H_2O$]. – ^{1}H NMR (300 MHz): δ = 1.54 (s, 3 H), 2.16 (s, 3 H), 2.34 (s, 3 H), 4.14 (s, 1 H), 7.13–7.18 (m, 4 H). – GC-MS (70 eV); *m/z* (%): 190 (526) [M^+], 189 (188), 147 (404), 119 (638), 105 (361), 104 (443), 103 (493), 91 (460), 78 (601), 43 (999). – FTIR (film): $\tilde{\nu}$ = 1716 cm^{-1} (C=O).

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