# 122. Diastereoselectivity and Reactivity in the *Diels-Alder* Reactions of α-Chloronitroso Ethers

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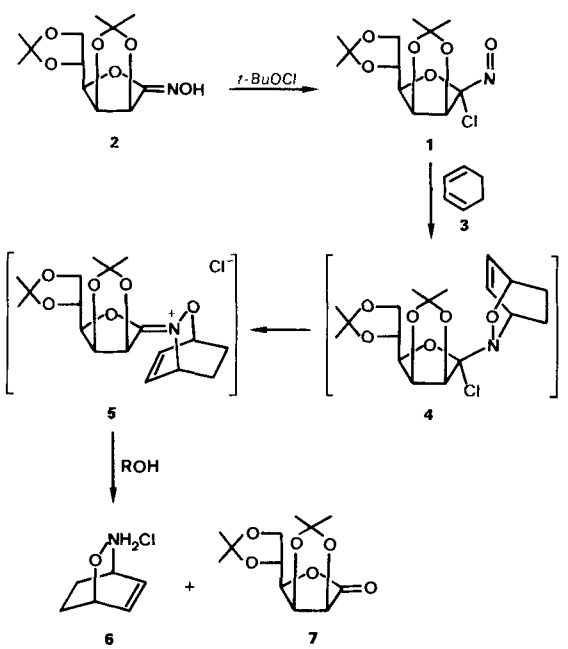
The structure of the α-chloronitroso ether **1**, obtained from the hydroximolactone **2** and *tert*-butyl hypochlorite (89%), was established by X-ray crystallographic analysis. The [4 + 2] cycloadditions of **1** with the dienes **3** and **8–11** led to the *N*-unsubstituted 3,6-dihydro-2*H*-1,2-oxazines **6** and **12–16** in high enantiomeric excess *(Table 1)*. Due to the additional α-alkoxy group, the reactivity of **2** is much superior to the one of known α-chloronitrosoalkanes. The reactive conformation of **1** was deduced from the X-ray analysis as well as the high diastereoselectivity of the cycloadditions. The importance of the α-alkoxy group was evidenced from the similar reactivity of the racemic α-chloronitroso ethers **25–27** which were prepared from the hydroximo ethers **28–30** and *tert*-butyl hypochlorite.

**Introduction.** – The [4 + 2]-cycloaddition of α-chloronitroso compounds to dienes allows an easy access to *N*-unsubstituted 3,6-dihydro-2*H*-1,2-oxazines [1] and hence to 1,4-aminoalcohols. The cycloaddition of achiral [2–6] chloronitroso compounds has been

*Scheme 1*

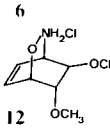
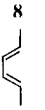
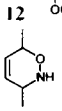
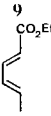
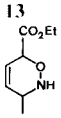


applied to the synthesis of natural products. Of particular interest to us is the synthesis of inosamine- and streptamine analogues[1]). Unfortunately, the instability of α-chloronitroso compounds requires low reaction temperatures and consequently long reaction times, thus limiting the scope of the cycloadditions. Therefore, more reactive, enantiomerically pure α-chloronitroso compounds are desired. In this context, we have studied the cycloadditions of 2,3:5,6-di-*O*-isopropylidene-1-*C*-nitroso-α-D-mannofuranosyl chloride (**1**). This chloronitroso ether is easily available from the hydroximolactone **2** [12] [13] and *tert*-butyl hypochlorite. The chloronitroso ether **1** proved to be quite stable and highly reactive towards 1,3-cyclohexadiene (**3**), leading *via* **4** and **5**[2]) to the bicyclic *N*-unsubstituted dihydrooxazine **6** (70%, ee ≥ 96%) [14] and the lactone **7** *(Scheme 1)*.

**Regio- and Stereoselectivity.** – Here, we report the experimental details of the cycloaddition of **1** to **3** and to the dienes **8–11** *(Table 1)*.

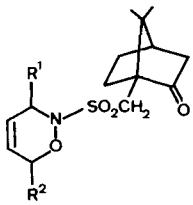
The additions to the cyclic dienes **3** and **8** [15] were carried out at −70° to give **6** (70%, ee ≥ 96%) and **12** (72%, ee ≥ 96%), respectively, within *ca.* 15 min. The acyclic dienes **9–11** were added to **1** at −20°. The reaction with **9** was completed within 4 h to give **13** [16] (69%, ee ≥ 96%), while the cycloaddition to ethyl sorbate (**10**) yielding **14** took 24 h (*cf.* [2]). The addition of unsymmetrically substituted 1,3-dienes may give two regioisomers [17] [18]. Generally, the C–N bond forms at the sterically less hindered end of a diene and at C(4) if C(1) carries an electron-withdrawing substituent. Thus, only the

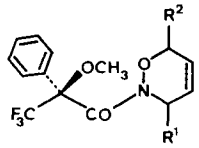
Table 1. *[4 + 2]-Cycloadditions of* **1** *to the Dienes* **3** *and* **8–11**

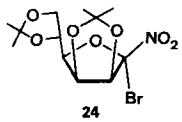
| Diene | Product | | Reaction temp. | Reaction time | Yield [%] | ee [%] |
|---|---|---|---|---|---|---|
|  **3** |  **6** | | −70° | ≤ 15 min | 70 | ≥ 96 |
|  **8** |  **12** | [a]) | −70° | ≤ 15 min | 72 | ≥ 96 |
|  **9** |  **13** | [a]) | −20° | ≤ 4 h | 69 | ≥ 96 |
|  **10** |  **14** | [a]) | −20° | ≤ 24 h | 63 | ≥ 96 |
|  **11** |  **15** +  **16** | [a])[b]) | −20° | ≤ 4 h | 68 | |

[a]) The absolute configuration was not determined so far.
[b]) The mixture of regioisomers could not be separated so far.

[1]) Intermediates for the synthesis of such analogues have been prepared using the cycloaddition of chloronitrosocyclohexane [7–10] and enantiomerically pure [11] chloronitroso compounds to cyclic dienes.
[2]) The nitrone hydrochloride **5** was either cleaved under the reaction conditions or during workup.







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| | | |
|---|---|---|
| 17 | $R^1, R^2 = -CH_2CH_2-$ | 20 |
| 18 | $R^1, R^2 = -CH(OCH_3)CH(OCH_3)-$ | 21 |
| 19 | $R^1 = R^2 = CH_3$ | 22 |
| | $R^1 = CH_3, R^2 = CO_2Et$ | 23 |

regioisomer **14** was isolated from the reaction of **1** with ethyl sorbate (**10**), while the addition to (*E*)-1,3-pentadiene (**11**) gave a 2:1 mixture of the regioisomers **15** and **16**, which, so far, could not be separated.

The diastereoselectivity of the cycloadditions was determined by establishing the enantiomeric purity of the dihydrooxazines using the following methods: *a*) esterification of the crude dihydrooxazines with (+)-camphor-10-sulfonyl chloride and integration of peaks of the individual diastereoisomers in the $^1$H-NMR spectra *(Table 2)*. *b*) Esterification of the crude dihydrooxazines with (*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropionyl chloride [19], separation of the diastereoisomeric esters by GC, and integration of the individual peaks *(Table 3)*. *c*) $^1$H-NMR spectroscopy of the dihydrooxazines

Table 2. AB *Systems in the $^1$H-NMR Spectrum* ($CDCl_3$) *of the (+)-Camphor-10-sulfonyl Derivatives of the Optically Active and the Racemic Dihydrooxazines*

| Compound | Optically active compound [ppm][a]) | Racemic compound [ppm] | ee [%] | Yield [%] |
|---|---|---|---|---|
| **17** | 3.54, 2.84 | 3.54, 2.84<br>3.44, 2.99 | ⩾ 96 | 88 |
| **18** | 3.62, 3.01 | 3.62, 3.01<br>3.59, 3.08 | ⩾ 96 | 96 |
| **19** | 3.86, 3.03 | 3.86, 3.03<br>3.65, 3.17 | ⩾ 96 | 95 |

[a]) Only one *AB* system was observed.

Table 3. *Retention Indices* ($R_I$) [38] [39] *of the* Mosher *Derivatives of the Optically Active and the Racemic Dihydrooxazines*

| Compound | Optically active compound $R_I$(I) | Racemic compound $R_I$(II) | ee [%] |
|---|---|---|---|
| **20** | | 1919 | ⩾ 98 |
| | 1954 | 1954 | |
| **21** | 2126 | 2126 | ⩾ 98 |
| | | 2134 | |
| **22** | | 1725 | ⩾ 98 |
| | 1732 | 1732 | |
| **23** | 1989 | 1989 | ⩾ 98 |
| | | 2009 | |

in the presence of chiral lanthanide shift reagents [20] [21]. Sharp signals were obtained from the dihydrooxazines **13** and **14**, which were enantiomerically pure.

Any of these methods suffices for the determination of the diastereoselectivity, however, case *a* and *b* demand a quantitative chemical yield or the exclusion of a possible enrichment of one diastereoisomer in the derivatisation reaction. To prove the absence of enrichment during the formation of the derivatives, we have treated the racemic dihydrooxazines obtained from the dienes and racemic α-chloronitroso compounds (see below) exactly in the same way as those obtained from **1**. The $^1$H-NMR spectra of a mixture of the diastereoisomeric camphor-10-sulfonamides show *AB* systems for $CH_2$(10), which are well-separated from each other. The crude camphor-10-sulfonamides **17** and **18**, derived from (±)-**6** and (±)-**12**, respectively, showed two *AB* systems of equal intensities. The ratio of the integrals of the *AB* systems of the camphor-10-sulfonamides **19**, derived from (±)-**13**, was 3:2, but the major diastereoisomer was not the one obtained from the enantiomerically pure **13**.

**Structure and Reactivity.** – The structure of **1** *(Fig. 1)* was established by X-ray diffraction analysis.

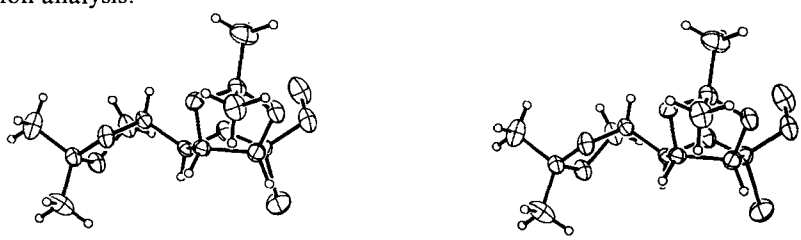


Fig. 1. *Stereoscopic representation* of **1**. The H-atoms are drawn with an arbitrary radius, the other atoms with thermal ellipsoids enclosing 50% probability.

The X-ray diffraction analysis was taken at 130 K of blue crystals from a $CHCl_3$ solution, space group $P6_1$, $a$ = 14.630(1) Å, $c$ = 13.929(1) Å. The asymmetric unit presumably contains some solvent besides one molecule of **1**. The intensities of 2611 symmetry-independent reflections within $\lambda^{-1}\sin\theta = 0.70$ Å were measured on a *Nicolet R3* diffractometer with low-temperature device *LT-1* in the $\omega$-scan mode using graphite monochromatized Mo$K_\alpha$ radiation and the usual corrections except for absorption were applied. Intensities $I$ below one half of their standard deviation $\sigma(I)$ were set to $I = 0.25\,\sigma(I)$. Both the space group and the lattice parameters gave rise of the assumption that the structure is isomorphous to 2,3:5,6-di-*O*-isopropylidene-1-*C*-nitro-α-D-mannofuranosyl bromide (**24**) of which an X-ray diffraction analysis has been published [22]. However, an attempt to expand our structure starting from the coordinates of that compound (without Br and $NO_2$) was unsuccessful at first, and initial coordinates were obtained from direct methods. During refinement it turned out that they could be approximately transformed into those of **24** by $x' = x$, $y' = x - y$ and $z' = 0.56 - z$. After transformation of the *Miller* indices by $h' = k$, $k' = h$ and $l' = \bar{l}$, the refinement was continued in the coordinate system of **24**. Although it was possible to locate all but three H-atoms in a difference electron density map after anisotropic refinement of the Cl-, C-, N-, and O-atoms, it was not possible to refine them all meaningfully. Therefore, the coordinates of the H-atoms belonging to the $CH_2$ and $CH_3$ groups were calculated, and in the further refinement they were allowed to ride on the C-atoms to which they belonged. The seven highest peaks of the difference density (0.88–0.71 e$^-$Å$^{-3}$), however, were not H-atoms but were located around the $6_1$ axis apart from the molecule. Because it was not possible to construct a solvent molecule from them, and because neither the NMR spectrum nor the elementary analysis had given an indication for $CHCl_3$, they were ignored. In the final blocked cascade refinement with about 100 variables per block, the 198 variables converged at $R = 0.079$ ($R_w = 0.070$) using all symmetry-independent reflections weighted by $w = (1 - \exp(-10\sin^2\theta/\lambda^2))/(\sigma^2(F) + 0.0008F^2)$. The absolute configuration was not determined but was taken for granted. For all computations the program SHELXTL [23] was used. Atom coordinates and temperature factors are given in *Table 4*.

Table 4. *Atom Coordinates* ($\times 10^4$) *and Temperature Factors* ($Å^2 \times 10^3$) *for* **1**

| Atom | *x/a* | *y/b* | *z/c* | $U_{eq}$[a]) |
|---|---|---|---|---|
| C(1) | 4248(3) | 2319(3) | 5788(2) | 29(1) |
| CL(1) | 3971(1) | 1352(1) | 6724(1) | 54(1) |
| N(1) | 4002(3) | 3091(3) | 6310(2) | 39(1) |
| O(1) | 4745(3) | 3929(3) | 6415(3) | 54(1) |
| C(2) | 3512(3) | 1803(3) | 4928(2) | 28(1) |
| O(2) | 3214(2) | 2517(2) | 4555(2) | 33(1) |
| C(3) | 4355(2) | 1756(2) | 4171(2) | 24(1) |
| O(3) | 4418(2) | 2565(2) | 3509(2) | 27(1) |
| C(4) | 5276(2) | 2090(2) | 4720(2) | 23(1) |
| O(4) | 5266(2) | 2768(2) | 5484(2) | 28(1) |
| C(5) | 6281(2) | 1703(2) | 4141(2) | 25(1) |
| O(5) | 6207(2) | 2036(2) | 3362(2) | 30(1) |
| C(6) | 7276(3) | 2910(3) | 4667(3) | 32(1) |
| O(6) | 7349(2) | 1992(2) | 4443(2) | 30(1) |
| C(7) | 3523(3) | 2706(3) | 3558(2) | 28(1) |
| C(8) | 2647(3) | 1919(3) | 2925(3) | 39(1) |
| C(9) | 3871(4) | 3835(3) | 3328(4) | 49(2) |
| C(10) | 6995(2) | 1737(2) | 3484(2) | 26(1) |
| C(11) | 7884(3) | 2350(4) | 2776(3) | 50(2) |
| C(12) | 6474(4) | 557(3) | 3365(4) | 52(2) |

[a]) Equivalent isotropic $U$ defined as one third of the trace of the orthogonalized $U$ tensor.

Apart from the changes in the substituents at C(1), the structure is almost identical with the one of **24** [22]. The conformation of the mannofuranose ring is intermediate between $^{O}T_4$ and $^{O}E$. The torsional angles Cl(1)–C(1)–O(4)–C(4) = 87.8(3)°, Cl(1)–C(1)–C(2)–C(3) = – 107.0(3)°, N(1)–C(1)–O(4)–C(4) = – 159.1(3)° and N(1)–C(1)–C(2)–C(3) = 141.5(3)° show that the Cl substituent adopts a pseudoaxial and the NO group a pseudoequatorial position. The O-atom of the NO group has a synperiplanar orientation to the ring O-atom (O(1)–N(1)–C(1)–O(4) = – 4.3(5)°, *cf. Fig. 1*). In *trans*-1,4-dichloro-1,4-dinitrosocyclohexane [24], the O-atom adopts a synperiplanar orientation to the Cl-atom. This synperiplanar orientation allows an interaction of the N lone pair and the $\sigma^*$ orbital of the polar bond (C–O or C–Cl) and may, thus, be interpreted as a kind of *'exo'*-anomeric effect [25] [26]. Since no evident steric interactions favour the observed synperiplanar arrangement of the NO group and the C(1)–O bond in **1**, it is most probably due to the higher electronegativity of the alkoxy substituent [24] [27]. The C–N distance in **1** is 1.530(6) and the N–O distance is 1.171(4) Å. In *trans*-1,4-dichloro-1,4-dinitrosocyclohexane, these distances are 1.505(7) and 1.139(5) Å, respectively. The C(1)–O bond (1.361(4) Å) is as short as in **24**. Similar shortened C(1)–O bonds are known from some 1-halopyranoses and related compounds with axial halogen atoms; they are accompanied by a lengthening of the C(1)–Hal bond and are commonly explained by a hyperconjugative interaction [28] [29]. Thus, in *cis*-2,3-dichlorodioxane, the bond length is 1.781(7) Å for the equatorial and 1.819(9) Å for the axial C–Cl bond. In **1**, the C–Cl bond length is 1.815(4) Å (dispersion correction for Cl [30] was taken into account, the C–Cl bond is 1.809(4) Å after refining the inverted structure). The shortening of the C(1)–O bond is possibly enhanced by the NO group. We have found similar short endocyclic C(1)–O bonds in 1-deoxy-1-nitrosugars [31]. The relatively large endo-

cyclic bond angle at C(1) (O(4)–C(1)–C(2) = 108.9(3)°) is in keeping with the presence of an anomeric effect. The angle N(1)–C(1)–Cl(1) = 101.0(2)° is even smaller than N(1)–C(1)–Br(1) in **24** [22]. As expected from steric reasons, the largest bond angle at C(1) is O(4)–C(1)–N(1) = 113.4(3)°. The angle C(1)–O(4)–C(4) = 106.2(2)° is somewhat smaller than the one found in some other furanoses, but has virtually the same value in **24**. The bond length C(4)–O = 1.460(4) Å is within the range found in other furanoses.

The striking features of **1** are its high reactivity and the high diastereoselectivity in the cycloadditions. The 1-chloro-1-nitrosocyclohexane reacted with cyclohexadiene (**3**) at – 20° over a period of 4 days and was unreactive towards ethyl sorbate (**10**)[3]). Under the same conditions, the chloronitroso ether **1** reacted instantly with **3** and within 24 h with **10** *(cf. Table 1)*. Trichloronitrosomethane [32] is similarly reactive as **1**. Evidently, the high reactivity of **1** is due to the presence of the two highly electronegative substituents at C(1). We presume that the conformation in which **1** crystallizes is the most reactive one *(cf. Fig. 1* and **A** in *Fig. 2)*. It may also be the lowest energy conformation [33]. The high diastereoselectivity of the cycloaddition speaks against a major participation of the alternative conformation **B** *(Fig. 2)* in which the NO group is synperiplanar to the C–Cl

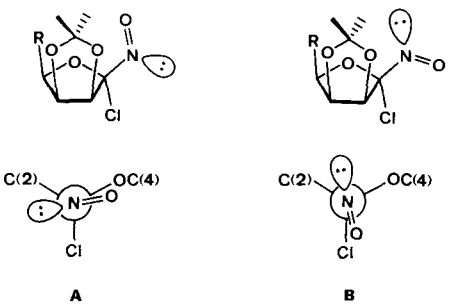



Fig. 2. *Possible conformations of the α-chloronitroso compound* **1**

bond (*cf.* discussion of the X-ray analysis) and where the N lone pair may interact with the $\sigma^*$ orbital of the C–Cl bond and the $\pi^*$ orbital of the NO group with the $\sigma^*$ orbital of the C–O bond. Space-filling models show that in the conformation **A**, one side of the NO group is sterically strongly hindered, while in the conformation **B** both sides of the NO group appear to be similarly accessible. The absolute configuration of the dihydrooxazine **6** is then only compatible with an approach of cyclohexadiene (**3**) where C(5) and C(6) of the diene are furthest removed from the carbohydrate moiety *(endo* addition, *cf. Fig. 3)*.

To prove the influence of the C(1) alkoxy group, we have prepared the α-chloronitroso ethers **25**–**27** from the hydroximo ethers **28**–**30** and *tert*-butyl hypochlorite

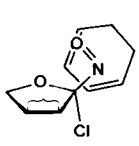
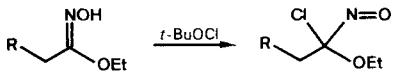



Fig. 3. endo-*Addition of* **1** *to the cyclohexadiene* (**3**)

[3]) A $CHCl_3$ solution of 1-chloro-1-nitrosocyclohexane and **10** at –20° did not react within 6 months.

*Scheme 2*




| | | |
|---|---|---|
| **28** | R = Cl | **25** |
| **29** | R = H | **26** |
| **30** | R = $CH_3$ | **27** |

*(Scheme 2)*. The hydroximo ethers **28–30** [34] [35] are easily available from the corresponding imidates [36]. The thermal stability of **25–27** is low and decreases in the sequence **25–27**. The solutions of the crude chloronitroso ethers **25–27**[4]), obtained from the stable hydroximo ethers **28–30** and *tert*-butyl hypochlorite, were used for the cycloadditions. The α-chloronitroso ethers **25–27** reacted with **3** at − 20° within 10 min and with **10** over a period of 2–3 days to give the racemic dihydrooxazines (±)-**6** and (±)-**14**, respectively in 50–70% yield. As expected, their reactivity is only slightly inferior to the one of **1**[5]) and much higher than the one of α-chloronitrosoalkanes. The preparation of **25–27** exemplifies a route to new, highly reactive α-chloronitroso compounds.

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## Experimental Part

*General.* See [37]. All reactions were carried out under dry $N_2$ using anh. solvents. $[\alpha]_D$: *Perkin-Elmer-141-MC* polarimeter, 1-dm cells. UV: *Phillips-PYE-UNICAM-SP-8-100* spectrometer, r.t. IR: *Perkin-Elmer-157* or *-257* spectrometer. NMR: *Bruker-WP-200* ($^1$H, 200 MHz) or *Jeol-JNM-FX-90* ($^{13}$C, 22.5 MHz). GC/MS: *Finnigan-MAT-112S*. Mikroanalyses: *Heräus EA 415/0* CHN analyser. GC: *Carlo-Erba-Fractovap-2350, OV-1* capillary column.

*2,3:5,6-Di-*O*-isopropylidene-1-*C*-nitroso-α-*D*-mannofuranosyl Chloride* (**1**). A soln. of *t*-BuOCl (4.36 g, 40.00 mmol) in $CH_2Cl_2$ (50 ml) was added dropwise at − 10° in the dark to a stirred soln. of *2,3:5,6-di-*O*-isopropylidene-*D*-mannonhydroximo-1,4-lactone* (**2**, 10.92 g, 40.00 mmol) in $CH_2Cl_2$ (100 ml). The mixture was stirred for further 15 min at − 10° and then evaporated to give crude product (12.03 g, 98%). Recrystallization from hexane gave **1** (10.93 g, 89%) as blue needles. M.p. 80°. $[\alpha]_D^{25}$ = − 1400° (*c* = 5.0, $CHCl_3$). UV(EtOH): 204(1218), 654(15). IR (KBr): 2995*m*, 2985*m*, 2970*m*, 1570*s*, 1385*s*, 1375*s*, 1260*s*, 1235*m*, 1215*s*, 1188*m*, 1155*m*, 1120*m*, 1070*s*, 1040*m*, 1005*m*, 975*m*, 965*w*, 955*w*, 925*w*, 895*m*, 850*s*, 820*m*, 760*w*. $^1$H-NMR: 5.55 (*d*, *J* = 5.6, H–C(2)); 5.01 (*dd*, *J* = 5.6, 3.5, H–C(3)); 4.55 (*ddd*, *J* = 8.2, 5.9, 4.1, H–C(5)); 4.24 (*dd*, *J* = 8.2, 3.5, H–C(4)); 4.12 (*ddd*, *J* = 9.1, 5.9, 4.1, 2 H–C(6)); 1.49 (*s*, $CH_3$); 1.40 (*s*, $CH_3$); 1.29 (*s*, 2 $CH_3$). $^{13}$C-NMR: 126.2 (*s*, C(1)); 113.8 (*s*, C(8)); 108.4 (*s*, C(7)); 88.2 (*d*, C(2)); 82.1 (*d*, C(3)); 78.7 (*d*, C(4)); 71.8 (*d*, C(5)); 65.3 (*t*, C(6)); 26.4 (*q*, $CH_3$); 25.0 (*q*, $CH_3$); 24.9 (*q*, $CH_3$); 24.1 (*q*, $CH_3$). Anal. calc. for $C_{12}H_{18}ClNO_6$ (307.73): C 46.84, H 5.90, N 4.55; found: C 47.01, H 5.89, N 4.31.

*Ethyl Chloroacetohydroximate* (**28**). The procedure of *Ketz* and *Zinner* [34] was modified as follows: a soln. of ethyl chloroacetimidate hydrochloride (15.70 g, 0.10 mol) in $Et_2O$ (100 ml) was added at 0° to a soln. of $K_2CO_3$ (41.42 g, 0.30 mmol) and $NH_2OH \cdot HCl$ (11.35 g, 0.15 mol) in $H_2O$ (100 ml). The mixture was stirred vigorously for 30 min. The aq. layer was extracted with $Et_2O$ (5 × 25 ml). The combined org. layers were dried ($MgSO_4$) and evaporated (bath temp. max. 25°). Recrystallization from petroleum ether gave **28** (9.32 g, 68%). M.p. 59–61°. IR: 3500–3100*s*, 2980*s*, 2940*s*, 2900*m*, 1650*s*, 1475*m*, 1445*m*, 1430*m*, 1380*m*, 1370*m*, 1325*s*, 1300*s*, 1255*s*, 1160*m*, 1120*w*, 1090*w*, 1040*s*, 995*s*, 895*s*. $^1$H-NMR: 6.10 (*s*, NOH); 4.21 (*s*, 2 H–C(2)); 4.05 (*q*, *J* = 7.0, $CH_3CH_2O$); 1.34 (*t*, *J* = 7.0, $CH_3CH_2O$). $^{13}$C-NMR: 160.5 (*s*, C=N); 63.5 (*t*, $CH_2O$); 33.6 (*t*, $CH_2Cl$); 14.2 (*q*, $CH_3$).

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[4]) Solutions of **25–27** in $CHCl_3$ are stable for several days.

[5]) This difference may reflect the influence of the substituents on the C(1) alkyl groups in **1** and **25–27**.

*Ethyl Acetohydroximate* (**29**) *and Ethyl Propiohydroximate* (**30**) were prepared analogously and purified by distillation.

**29**: 6.70 g, 65%. B.p. 60°/14 Torr. M.p. 27–28°. IR: 3600–3000*m*, 2985*s*, 2950*s*, 2910*m*, 1655*s*, 1485*m*, 1470*m*, 1445*m*, 1370*m*, 1340*s*, 1300*s*, 1245*s*, 1175*w*, 1160*w*, 1120*m*, 1090*s*, 1075*s*, 1040*s*, 1005*s*, 975*s*, 900*w*, 865*m*. $^1$H-NMR: 8.56 (*s*, NOH); 3.98 (*q*, *J* = 7.0, $CH_3CH_2O$); 1.98 (*s*, 3 H–C(2)); 1.26 (*t*, *J* = 7.0, $CH_3CH_2O$). $^{13}$C-NMR: 163.2 (*s*, C=N); 62.4 (*t*, $CH_2$); 14.4 (*q*, $CH_3$); 13.1 (*q*, $CH_3$).

**30**: 6.90 g, 59%. B.p. 67°/13 Torr. IR: 3500–3100*s*, 2985*s*, 2950*s*, 2910*m*, 1655*s*, 1470*m*, 1445*m*, 1380*m*, 1375*m*, 1340*m*, 1320*s*, 1300*m*, 1250*s*, 1090*s*, 1075*s*, 1040*s*, 1005*s*, 975*s*. $^1$H-NMR: 7.88 (*s*, NOH); 3.97 (*q*, *J* = 7.0, $CH_3CH_2O$); 2.44 (*q*, *J* = 7.6, 2 H–C(2)); 1.29 (*t*, *J* = 7.0, $CH_3CH_2O$); 1.12 (*t*, *J* = 7.6, 3 H–C(3)). $^{13}$C-NMR: 180.0 (*s*, C=N); 70.6 (*t*, $CH_2$); 20.9 (*t*, $CH_2$); 13.6 (*q*, $CH_3$); 9.8 (*q*, $CH_3$).

*(1,2-Dichloro-1-nitrosoethyl) Ethyl Ether* (**25**). A soln. of *t*-BuOCl (2.17 g, 20.00 mmol) in $CHCl_3$ (20 ml) was added dropwise at – 30° in the dark to a stirred soln. of **28** (2.74 g, 20.00 mmol) in $CHCl_3$ (30 ml) and the mixture was stirred for further 15 min at this temp. For further reactions, this soln. was used directly. *(1-Chloro-1-nitroso-ethyl) ethyl ether* (**26**) and *(1-chloro-1-nitrosopropyl) ethyl ether* (**27**) were prepared analogously. For $^1$H-NMR spectroscopy, **25–27** were prepared in NMR tubes (1 mM $CDCl_3$ soln.). **25**: 4.08 (*m*, $CH_3CH_2O$, 2 H–C(2)); 1.61 (*s*, OH); 1.43 (*t*, $CH_3CH_2O$); 1.29 (*s*, *t*-BuOH). **26**: 4.07 (*q*, *J* = 7.0, 1 H, $CH_3CH_2O$); 4.05 (*q*, *J* = 7.0, 1 H, $CH_3CH_2O$); 1.58 (*s*, 3 H–C(2)); 1.60 (*s*, OH); 1.39 (*t*, *J* = 7.0, $CH_3CH_2O$); 1.27 (*s*, *t*-BuOH). **27**: 4.12 (*q*, *J* = 7.0, 1 H, $CH_3CH_2O$); 4.11 (*q*, *J* = 7.0, 1 H, $CH_3CH_2O$); 1.96 (*q*, *J* = 7.4, 2 H–C(2)); 1.60 (*s*, OH); 1.36 (*t*, *J* = 7.0, $CH_3CH_2O$); 1.28 (*s*, *t*-BuOH); 0,94 (*t*, *J* = 7.4, 3 H–C(3)). As indicated by $^1$H-NMR, **25–27** were obtained in quantitative yields.

*(1S,4R)-3-Aza-2-oxabicyclo[2,2,2]oct-5-ene Hydrochloride* (**6**). Diene **3** (1.60 g, 20.00 mmol) and EtOH (10 ml) were added at – 70° to a soln. of **1** (3.07 g, 10.00 mmol) in $CHCl_3$ (30 ml), and the mixture was kept at – 70°, until the blue colour of **1** had disappeared. The soln. was then extracted with $CHCl_3$, the extracts treated with 1N HCl, and the HCl soln. evaporated to give crude crystalline **6** (1.22 g, 83%). Recrystallization from EtOH gave pure **6** (1.03 g, 70%). M.p. 135° (dec.). $[\alpha]_D^{25}$ = + 24.4° (*c* = 5.0, $CHCl_3$). IR (KBr): 3600–3300*m*, 3025–2330*s*, 1540*s*, 1452*m*, 1415*s*, 1381*s*, 1359*m*, 1310*w*, 1280*m*, 1265*m*, 1220*m*, 1164*w*, 1120*w*, 1080*w*, 1058*s*, 1022*w*, 1005*w*, 988*w*, 959*m*, 940*s*, 920*s*, 856*s*, 810*m*, 798*m*, 773*s*, 661*s*, 650*m*. $^1$H-NMR($D_2O$): 6.90 (*ddd*, *J* = 8.4, 5.8, 1.5, H–C(6)); 6.63 (*ddd*, *J* = 8.4, 6.3, 1.5, H–C(5)); 5.01 (*ddd*, *J* = 5.8, 3.8, 1.5, H–C(1)); 4.60 (*ddd*, *J* = 6.3, 3.5, 1.5, H–C(4)); 2.25 (*m*, $H_{exo}$–C(7)); 2.16 (*m*, $H_{exo}$–C(8)); 1.60 (*m*, $H_{endo}$–C(7), $H_{endo}$–C(8)). $^{13}$C-NMR($D_2O$): 138.7 (*d*, C(6)); 130.6 (*d*, C(5)); 74.0 (*d*, C(1)); 51.6 (*d*, C(4)); 23.9 (*t*); 19.2 (*t*). Anal. calc. for $C_6H_{10}ClNO$ (147.60): C 48.83, H 6.83, N 9.49; found: C 48.80, H 7.04, N 9.58.

*(–)-(1R*,4S*,7R*,8S*)-Dimethoxy-3-aza-2-oxa-bicyclo[2,2,2]oct-5-ene Hydrochloride* (**12**)[6]. Diene **8** was treated analogously (see **6**) to obtain crude **12** (1.66 g, 80%). Recrystallization from EtOH gave pure **12** (1.50 g, 72%). M.p. 165° (dec.). $[\alpha]_D^{25}$ = – 22.4° (*c* = 5.0, $CHCl_3$). IR (KBr): 3650–3250*m*, 3000–2500*m*, 1620*w*, 1550*w*, 1450*w*, 1380*m*, 1326*w*, 1270*w*, 1220–1200*m*, 1115–1100*s*, 1165*w*, 1035–1020*w*, 970*m*, 942*w*, 918*m*, 850*m*, 825*s*, 740*m*, 691*m*, 625*m*. $^1$H-NMR($D_2O$): 6.68 (*ddd*, *J* = 8.1, 5.5, 1.5, H–C(6)); 6.52 (*ddd*, *J* = 8.1, 6.6, 1.5, H–C(5)); 5.02 (*ddd*, *J* = 5.5, 4.2, 1.5, H–C(1)); 4.82 (*ddd*, *J* = 6.6, 2.7, 1.5, H–C(4)); 3.62 (*dd*, *J* = 4.2, 1.5, H–C(7)); 3.36 (*m*, H–C(8)); 3.35 (*s*, $CH_3O$); 3.27 (*s*, $CH_3O$). $^{13}$C-NMR($D_2O$): 137.1 (*d*, C(6)); 130.1 (*d*, C(5)); 79.7 (*d*, C(7), C(8)); 73.1 (*d*, C(1)); 59.5 (*q*, 2 $CH_3O$); 54.9 (*d*, C(4)). Anal. calc. for $C_8H_{16}ClNO_3$ (207.66): C 46.27, H 6.79, N 6.75; found: C 46.14, H 6.67, N 7.02.

*(–)-3,6-Dihydro-3,6-dimethyl-2H-1,2-oxazine* (**13**)[6]. A soln. of **9** (2.02 g, 25.00 mmol) in $CH_2Cl_2$ (10 ml) was added at – 20° to a soln. of **1** (1.63 g, 5.00 mmol) in $CH_2Cl_2$ (20 ml) and EtOH (5 ml). The mixture was kept at this temp., until the blue colour had disappeared and was then extracted with $H_2O$ (2 × 20 ml) and 1N HCl (20 ml). The aq. layer was neutralized with $KHCO_3$ and extracted with $CH_2Cl_2$ (3 × 20 ml). The extracts were dried ($MgSO_4$), filtered, and evaporated to obtain crude **13** (0.52 g, 92%). Destillation gave pure **13** (0.39 g, 69%). B.p. 48°/14 Torr. $[\alpha]_D^{25}$ = – 52.9° (*c* = 0.5, $CH_2Cl_2$). IR: 3670*w*, 3300*w*, 3030*w*, 2980*s*, 2930*m*, 2890*w*, 2870*w*, 2840*w*, 2540*w*, 2460*w*, 1675*w*, 1600*w*, 1448*m*, 1420*w*, 1388*w*, 1370*s*, 1316*w*, 1300*w*, 1240–1200*w*, 1150*w*, 1130*m*, 1113*w*, 1100*w*, 1089*s*, 1065*w*, 1044*s*, 1000*m*, 935*m*, 868*w*, 851*w*, 832*m*, 800–700*w*, 660*w*. $^1$H-NMR: 5.85 (*ddd*, *J* = 10.3, 3.4, 2.0, H–C(4)); 5.72 (*ddd*, *J* = 10.3, 2.3, 1.7, H–C(5)); 4.33 (*dddq*, *J* = 6.6, 2.3, 2.2, 2.0, H–C(6)); 3.50 (*dddq*, *J* = 6.8, 3.4, 2.2, 1.7, H–C(3)); 1.23 (*d*, *J* = 6.6, $CH_3$); 1.24 (*d*, *J* = 6.8, $CH_3$). $^{13}$C-NMR: 129.5 (*d*, C(4), C(5)); 71.9 (*d*, C(6)); 50.9 (*d*, C(3)); 19.4, 19.0 (2*q*, C(7), C(8)). EI-MS: 113 (18, $M^{+\cdot}$), 98 (38), 96 (5), 94 (6), 84 (7), 82 (40), 81 (20), 80 (9), 79 (5), 70 (7), 69 (5), 68 (9), 67 (100), 56 (9), 55 (9), 54 (15), 53 (14), 43 (30), 42 (26), 41 (24), 39 (15). Anal. calc. for $C_6H_{11}NO$ (113.16): C 63.68, H 9.80, N 12.37; found: C 63.48, H 9.69, N 12.71.

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[6]) The absolute configuration has not been determined so far.

*(+)-Ethyl 3,6-Dihydro-3-methyl-2*H*-1,2-oxazine-6-carboxylate* (**14**)[6]. The reaction of **10** was carried out as described above (see **13**), but instead of 1N HCl $H_2O$ was used for extraction to give crude **14** (0.75 g, 88%). Distillation gave pure **14** (0.54 g, 63%). B.p. 116°/11 Torr. $[\alpha]_D^{25} = +133.2°$ (*c* = 5.0, $CHCl_3$). IR: 3670*w*, 3455*m*, 3250*w*, 3030*m*, 2980*s*, 2938*s*, 2910*m*, 2888*w*, 2460*w*, 1740*s*, 1644*w*, 1620*w*, 1490*s*, 1452*m*, 1448*m*, 1420*w*, 1370*s*, 1330*s*, 1319*s*, 1262*s*, 1245–1190*m*, 1160*s*, 1110*m*, 1080*s*, 1054*m*, 1023*s*, 970*w*, 956*w*, 930*w*, 864*w*, 843*w*, 820–688*w*, 660*w*. $^1$H-NMR: 6.00 (*m*, H–C(4),H–C(5)); 5.72 (br. *m*, NH); 4.65 (*m*, H–C(6)); 4.25 (*q*, *J* = 7.1, $CH_3CH_2O$); 3.82 (*m*, H–C(3)); 1.31 (*t*, *J* = 7.1, $CH_3CH_2O$); 1.09 (*d*, $CH_3$–C(3)). $^{13}$C-NMR: 170.8 (*s*, C=O); 133.0 (*d*); 121.8 (*d*, C(4),C(5)); 72.7 (*d*, C(6)); 61.3 (*t*, $CH_2$); 50.5 (*d*, C(3)); 16.8 (*q*, $CH_3$); 14.2 (*q*, $CH_3$). EI-MS: 171 (24, $M^{+\cdot}$), 156 (18), 141 (17), 125 (11), 113 (8), 98 (65), 97 (21), 95 (16), 84 (6), 83 (10), 82 (23), 70 (6), 69 (5), 68 (6), 67 (24), 66 (5), 57 (38), 55 (24), 54 (9), 53 (11), 44 (9), 43 (18), 42 (100), 41 (28), 39 (17).

*3,6-Dihydro-6-methyl-2*H*-1,2-oxazine* (**15**) *and 3,6-Dihydro-3-methyl-2*H*-1,2-oxazine* (**16**). Diene **11** was treated as described above (see **13**) yielding a 2:1 mixture **15**/**16** (0.48 g, 85%). Distillation gave pure **15**/**16** (2:1, 0.34 g, 68%). B.p. 43°/11 Torr. IR: 3670*w*, 3600–3150*w*, 3040*m*, 2980*s*, 2930*m*, 2875*m*, 2840*m*, 2600–2400*w*, 1600*w*, 1444*m*, 1424*m*, 1385*w*, 1372*s*, 1341*w*, 1311*w*, 1250–1200*m*, 1180*w*, 1135*m*, 1100*s*, 1083*m*, 1060*m*, 1035*s*, 1020*m*, 1003*w*, 991*w*, 965*w*, 940*m*, 900*m*, 848*w*, 810–700*m*, 680–660*m*. $^1$H-NMR: 5.90–5.72 (*m*, H–C(4),H–C(5)); 5.42 (*s*, NH); 4.39 (*m*, H–C(6), **15**); 3.72 (*m*, H–C(3), **16**); 4.29, 4.25, 4.19, 3.60, 3.32, 3.28 (each *m*, 2 H, 2 H–C(3), **15**, 2 H–C(6), **16**); 1.19 (*d*, 3 H–C(7), **15**); 1.11 (*d*, 3 H–C(7), **16**). $^{13}$C-NMR: 129.6, 129.0, 123.9, 123.2 (4*d*, C(4),C(5)); 71.2 (*d*, C(6), **15**); 66.5 (*t*, C(3), **15**); 50.1 (*d*, C(3), **16**); 45.9 (*t*, C(6), **16**); 18.4 (*q*, $CH_3$–C(6), **15**); 16.9 (*q*, $CH_3$–C(3), **16**). GC/MS (EI): **15**: 99 (32, $M^{+\cdot}$), 84 (7), 82 (17), 80 (7), 70 (18), 68 (64), 67 (100), 65 (5), 57 (5), 56 (9), 55 (13), 54 (8), 53 (26), 43 (22), 42 (13), 41 (24), 40 (6), 39 (18). **16**: 99 (22, $M^{+\cdot}$), 98 (5), 85 (5), 84 (100), 70 (5), 68 (29), 67 (53), 57 (5), 56 (7), 55 (5), 54 (7), 53 (17), 43 (6), 42 (28), 41 (20), 39 (17).

*(±)-6 and (+)-***12***–(±)-***16**. A 5-fold excess of the diene and a 10-fold excess of EtOH was added to the reaction mixture of **28** (without isolation) at –30° in the dark, and the mixture was kept at –30°, until the blue colour had disappeared. Normal workup (see above) gave (±)-**6** (68%), (±)-**12** (65%), (±)-**13** (59%), (±)-**14** (52%), and (±)-**15**/**16** (2:1, 56%). The $^1$H-NMR spectra were identical with those of the optically active **6** and **12**–**6**.

*(+)-Camphor-10-sulfonylamides* **17**–**19**. *General Procedure.* A soln. of (+)-camphor-10-sulfonyl chloride (0.25 g, 1.00 mmol) in $CCl_4$ (10 ml) was added during 1 h to a stirred soln. of the dihydrooxazine[7]) (1 mmol) and 4-(dimethylamino)pyridine (1.12 g, 1 mmol) in $CCl_4$ (5 ml) at 50°. The mixture was stirred for further 2 h at 50° and then 2 d at r.t. After filtration, the soln. was washed successively with each 5 ml of dil. HCl, $K_2CO_3$, and 5% NaCl, dried ($MgSO_4$), filtered, and evaporated to give crystalline products.

*10-[(1′*S*,4′*R*)-(3′-Aza-2′-oxabicyclo[2.2.2]oct-5′-en-3′-yl)sulfonyl]camphor* (**17**; 88%): M.p. 130–131°. $[\alpha]_D^{20} = +60.5$ (*c* = 1.6, $CH_2Cl_2$). IR (KBr): 3010*m*, 2970*s*, 2940*s*, 2938*s*, 1738*s*, 1470*w*, 1455*w*, 1440*w*, 1420*w*, 1408*w*, 1382*m*, 1350*s*, 1310*w*, 1276*m*, 1270*m*, 1220*w*, 1190*w*, 1156*s*, 1130*w*, 1065*m*, 1055*s*, 1030*w*, 1000*m*, 982*m*, 965*m*, 948*s*, 880*w*, 868*s*, 820*s*, 800*m*, 775*s*, 745*w*, 735*m*, 700*m*, 670*m*, 640*s*. $^1$H-NMR: 6.62 (*m*, H–C(5′),H–C(6′)); 4.84 (*m*, H–C(1′)); 4.70 (*m*, H–C(4′)); 3.54 (*A* of *AB*, *J* = 14.6, H–C(10)); 2,84 (*B* of *AB*, *J* = 14.6, H–C(10)); 2.60–1.60 (*m*, 11 H); 1.13 (*s*, $CH_3$); 0.89 (*s*, $CH_3$). $^{13}$C-NMR: 214.3 (*s*, C=O); 132.3, 130.5 (2*d*, C(5′),C(6′)); 71.2 (*d*, C(1′)); 58.5 (*s*, C(1)); 49.3 (*d*, C(4′)); 47.6 (*s*, C(7)); 47.6 (*t*); 42.8 (*d*, C(4)); 42.5 (*t*); 26.9 (*t*); 25.1 (*t*); 23.0 (*t*); 21.6 (*t*); 20.1 (*q*); 19.7 (*q*). Anal. calc. for $C_{16}H_{23}NO_4S$ (325.43): C 59.05, H 7.12, N 4.30; found: C 59.18, H 7.29, N 4.34.

*10-[(1′*R**, 4′*S**, 7′*R**, 8′*S**)-(7′,8′-Dimethoxy-3′-aza-2-oxabicyclo[2.2.2]oct-5′-en-3′-yl)sulfonyl]camphor* (**18**; 96%): $^1$H-NMR: 6.56 (*m*, H–C(5′),H–C(6′)); 5.00 (*m*, 1 H); 4.87 (*m*, 1 H); 3.62 (*d*, *J* = 14.6, H–C(10)); 3.60 (*m*, 1 H); 3.47 (*s*, $CH_3O$); 3.40 (*s*, $CH_3O$); 3.19 (*m*, 1 H); 3.01 (*B* of *AB*, *J* = 14.6, H–C(10)); 2.45–1.19 (*m*, 7 H); 1.11 (*s*, $CH_3$); 0.89 (*s*, $CH_3$). *10-(3′,6′-Dihydro-3′,6′-dimethyl-2′*H*-1′,2′-oxazin-2′-yl)camphor* (**19**; 95%): $^1$H-NMR: 5.82 (*ddd*, *J* = 10.2, 4.6, 2.1), 5.70 (*dt*, *J* = 10.2, 1.5, H–C(4′),H–C(5′)); 4.85 (*dq*, *J* = 6.8, 2.1), 4.35 (*m*, H–C(3′),H–C(6′)); 3.86 (*A* of *AB*, *J* = 15.3, H–C(10)); 3.03 (*B* of *AB*, *J* = 15.3, H–C(10)); 2.54–1.43 (*m*, 7 H); 1.41 (*d*, *J* = 6.5); 1.32 (*d*, *J* = 6.8, $CH_3$–C(3′), $CH_3$–C(6′)); 1.15 (*s*, $CH_3$); 0.90 (*s*, $CH_3$).

*(S)-3,3,3-Trifluoro-2-methoxy-2-phenylpropionyl Derivatives* **20**–**23** *for GC Studies.* The reaction was carried out in a dry test tube (5 × 50 mm) fitted with a rubber septum. The reagents were injected *via* syringe in the following order: dihydrooxazine[7]) (0.10 mmol) in $CCl_4$ (150 µl), pyridine (11,06 mg, 0.14 mmol), and (*S*)-3,3,3-trifluor-2-methoxy-2-phenylpropionyl chloride (35.04 mg, 0.14 mmol) in $CCl_4$ (150 µl). The mixture was shaken at r.t., until the reaction was complete as evidenced by GC. At the end, the mixture was washed successively with each 300 µl of diluted HCl, $KHCO_3$, and $H_2O$. Then, 10 µl from the $CCl_4$ layer were diluted in 2 ml of $Et_2O$, and the GC was taken from this soln. (temp. 80° (1 min), 80–260° (6°/min), 260° (10 min); $R_I$ values relative to alkane mixture, $C_{10}$–$C_{30}$ [38] [39]).

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[7]) The free dihydrooxazines were obtained from **6** and **12** by treatment with 10% $Na_2CO_3$ soln. and extraction with $CCl_4$. The extracts were dried and evaporated.

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