[4 + 2] Cycloadditions of Nitroalkenes in Water. Highly Asymmetric Synthesis of Functionalized Nitronates

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Received February 16, 2001

The [4 + 2] cycloadditions of (*E*)-2-aryl-1-cyano-1-nitroalkenes **1** with achiral and enantiopure vinyl ethers **2** and **3** carried out in sole water are reported. These reactions occur in a heterogeneous phase under mild conditions and are fast and highly stereoselective. By using (−)-*N*,*N*-dicyclohexyl-(1*S*)-isoborneol-10-sulfonamide as a chiral auxiliary, the cycloadditions are totally asymmetric. The face selectivity is discussed in terms of the shape of the chiral auxiliary and the reactive conformation of vinyl ether.

Cyclic six-membered nitronates are interesting synthetic intermediates easily obtained by [4 + 2] cycloaddition of α,β-unsaturated nitroalkenes (acting as 4π components)[1] with enamines,[2] silyl enol ethers,[3] enolate anions,[4] silyl ketene acetals,[5] allylsilanes,[6] and simple alkenes[7] and can be converted into a variety of compounds such as nitroalkylated enamines,[2] 1,4-diones,[3] pyrrolidines,[8] aminocyclopentanes,[9] *N*-oxy-β-lactams,[10] and highly functionalized polyheterocyclic systems.[11]

The cycloaddition chemistry of nitroalkenes has been widely investigated by Denmark.[8,11a−c,12,13a,b] These reactions are conveniently carried out in organic solvent (CH_2Cl_2, PhMe, PhH) at low temperature (−78 °C) and in the presence of Lewis acids ($TiCl_4$, $TiBr_3$(O*i*-Pr), $SnCl_4$, MAD, MAPh, ATPh).[11a−c,13] Without catalyst the reaction requires a large excess of dienophile,[13c,14] a long reaction time, or activated nitroalkenes.[15] The use of high pressure allows some of these difficulties to be overcome, at least for the cycloadditions of nitrostyrenes to enol ethers.[10,11d]

Thermal and catalyzed asymmetric nitroalkene [4 + 2] cycloadditions in organic solvent have also been investigated by using either optically active nitroalkenes[16] or enantiopure vinyl ethers.[8b,9]

For some years we have been interested in organic reactions performed in pure water as reaction medium, and we have shown that the aqueous medium can strongly favor the reactivity and selectivity of the reaction even when it is carried out under heterogeneous conditions.[17]

[4 + 2] Cycloadditions between an electron-rich diene with an electron-deficient dienophile have been widely investigated in aqueous medium,[18] while, to our knowledge, only two examples are reported in the literature concerning [4 + 2] cycloadditions in water between an electron-deficient diene and an electron-rich dienophile:

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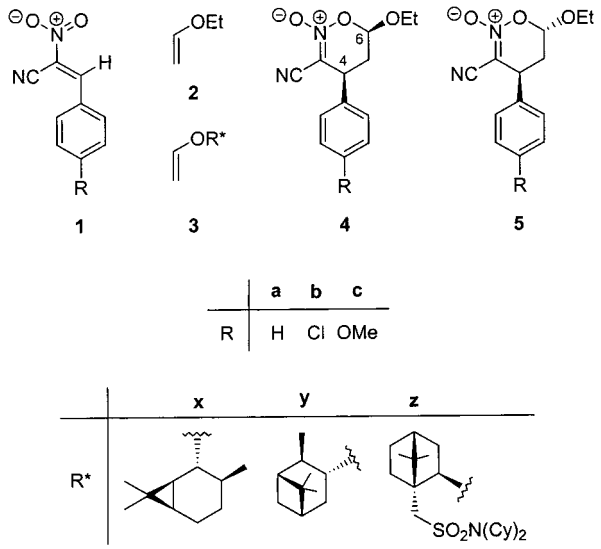
10.1021/jo010182v CCC: $20.00
Published on Web 05/31/2001

Scheme 1



the cycloadditions of di(α-pyridyl)-1,2,4,5-tetrazine with para-substituted styrenes,[19] and the cycloadditions of (*E*)-1,2-diaza-1,3-butadienes with enol ethers, phenyl vinyl sulfide, and cyclopentadiene.[20]

As part of our program of organic synthesis in water, we are interested in demonstrating the potentiality of aqueous medium in the [4 + 2] cycloaddition of nitroalkenes working either as 4π or 2π components. Here we report the results of [4 + 2] cycloaddition of (*E*)-2-aryl-1-cyano-1-nitroalkenes **1** with ethyl vinyl ether **2** and enantiopure vinyl ethers **3**, performed in pure water and in organic solvent for comparison.

Results and Discussion

2-Aryl-1-cyano-1-nitroalkenes **1** (Scheme 1) are reactive compounds that are easily accessible in pure form.[21a,b] Their chemistry has been little-studied,[21] and they have never been used in [4 + 2] cycloadditions. The results of cycloaddition reactions of **1** with **2** in water and CH_2Cl_2 are reported in Table 1. All the reactions are totally regioselective and highly diastereoselective. The reactions carried out in aqueous medium occur in heterogeneous phase and are slower than those performed in homogeneous solution in organic solvent, but high selectivity and high reaction yields were achieved just the same. The [4 + 2] cycloadditions can be regarded as totally *endo* diastereoselective because the amount of *trans* adducts **5**, which, in principle, originated from *exo*-type additions, is probably the result of the epimerization at C-6 of kinetically favored *cis* adducts **4**. This nitronate epimerization was mentioned previously,[8b] and we have observed that by maintaining the pure adduct **4b** in acetone at 40 °C for 15 min, adduct **5b** is produced. The rate of epimerization of the acetal center depends on the solvent and is accelerated by heating. The *cis*−*trans* epimerization causes problems in the purification of the reaction products by recrystallization, but it is not important in the elaboration of nitronate for synthetic purposes because the stereogenic acetal center is removed.

Table 1. [4 + 2] Cycloadditions of Nitroalkenes 1 with Ethyl Vinyl Ether 2

				product (%)		
nitroalkene	medium	*T* (°C)	*t* (m)	**4**	**5**	yield (%)[a]
1a	H_2O	0	3	80	20	75
1a	CH_2Cl_2	0	2	90	10	82
1b	H_2O	0	20	96	4	90
1b	CH_2Cl_2	0	5	95	5	90
1c	H_2O	rt	10	98	2	85
1c	CH_2Cl_2	rt	5	97	3	85

[a] Yield of isolated main reaction product.

The *endo* diastereoselectivity of the reaction is justified on the basis of the strong secondary orbital interactions between the oxygen of electron-rich vinyl ether **2** and the positively charged nitrogen atom of nitroalkene **1** which is present in the *endo* transition state and absent in the *exo*-mode orientation.

The *cis*−*trans* configuration of nitronates **4** and **5** has been assigned on the basis of ^{1}H NMR coupling constant values and NOE experiments. This procedure was also followed for the other nitronates **6**−**9** (see below). The data recorded for *cis* nitronate **4b** are illustrated as an example.

The saturation of H_6 proton frequency gives a NOE effect on protons H_4 (2%), $H_{5\alpha}$ (6.1%), and $H_{5\beta}$ (0.9%) and the saturation of the H_4 proton frequency gives a NOE effect on H_6 (2.3%) and $H_{5\alpha}$ (6.1%), but no NOE effect was observed on $H_{5\beta}$. The protons H_4, H_6, and $H_{5\alpha}$ are therefore *cis* to each other. The vicinal coupling constant values of proton H_6 and H_5 [$J(H_6-H_{5\beta}) = 4.6$ Hz; $J(H_6-H_{5\alpha}) = 4.0$ Hz] indicate that the proton at C-6 is pseudoequatorial, and the high value of the vicinal coupling constant of protons H_4 and $H_{5\beta}$ [$J(H_4-H_{5\beta}) = 7.1$ Hz] and the absence of NOE effect between the two protons suggest a pseudoaxial position for H_4.

The configurations of **4** and **5** are further supported by epimerization of **4** to **5** as mentioned above and from X-ray analyses of optically active nitronates (see below).

The ^{1}H NMR data, for many *cis* and *trans* nitronates, collected in the course of this study (Table S1, see Supporting Information), are diagnostic and allow simple rules to be defined for determining the *cis* or *trans* configurations of nitronate-like **4** and **5**: (a) the signals for $H_{5\alpha}$ and H_6 of *cis* isomer are at lower field than those for the *trans* one; (b) the $\Delta(\delta_{5\alpha} - \delta_{5\beta})$ is higher for the *cis* than for the *trans* isomer: ≅0.7 and ≅0.15 ppm, respectively; (c) the $J(H_6-H_{5\alpha})$ and $J(H_6-H_{5\beta})$ are higher for the *cis* than for the *trans* nitronates (3.6−4.9 vs 2.0−2.3 Hz and 4.5−5.1 vs 2.2−2.7 Hz, respectively); and (d) the $J(H_4-H_{5\beta})$ is higher for the *trans* than for the *cis* adducts (11.6−11.9 vs 6.3−8.1 Hz).

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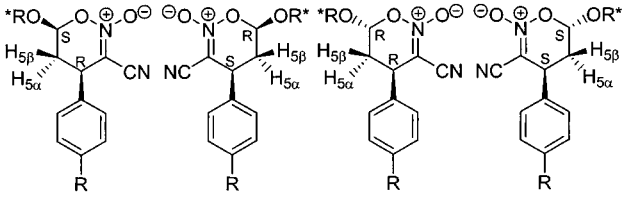
Table 2. Asymmetric [4 + 2] Cycloadditions of Nitroalkenes 1 with Enantiopure Vinyl Ethers 3 in Pure Water

	products (%)[d]					
reactants	**6**	**7**	**8**	**9**	*endo/exo*	de (4*R*) %
1b + **3x**[a]	54	35	5	6	89:11	18
1b + **3y**[a]	60	30	5	5	90:10	30
1a + **3z**[b]	85		15		85:15	100
1b + **3z**[c]	85		15		85:15	100
1c + **3z**[b]	83		17		83:17	100

[a] At 0 °C for 30 min. [b] At rt for 60 min. [c] At 0 °C for 60 min. [d] For the yield of isolated products see Experimental Section.

Scheme 2



The asymmetric cycloaddition of nitroalkenes **1** in pure water was explored by using enantiopure vinyl ethers (+)-**3x**, (+)-**3y**, and (−)-**3z**. The cycloaddition of **1b** with (+)-2-isocaranyl vinyl ether (**3x**) in water was completed in 30 min at 0 °C and produced a 89:11 mixture of *endo* and *exo* adducts (Table 2). The *endo* diastereoisomers (+)-**6bx** and **7bx** which constituted 54% and 35% of the mixture and adducts **8bx** and **9bx**, that accounted for 5% and 6%, respectively, are probably the epimerization products of **6bx** and **7bx**, respectively (Scheme 2). The 54:35:5:6 ratio, therefore, reflects a 59:41 (4*R*/4*S*) ratio of diastereoisomers or a 18% de (4*R*). Only the adduct (+)-**6bx** was isolated in pure form; the other three stereoisomers were characterized by using an enriched mixture.

The cycloaddition of **1b** with (+)-isopinocampheyl vinyl ether (**3y**) gave similar results: the 60:30:5:5 ratio of nitronates **6by**, (+)-**7by**, (+)-**8by**, and **9by** reflects a 9:1 *endo/exo* ratio and a 65:35 (4*R*/4*S*) ratio of diastereoisomers or a 30% de (4R). Also in this case, the nitronates (+)-**8by** and **9by** came from the epimerization of **6by** and (+)-**7by**, respectively, rather than from an *exo* addition.[22] The adducts (+)-**7by** and (+)-**8by** were isolated in pure form; while **6by** and **9by** were characterized by using enriched mixtures.

By reacting **1b** with the vinyl ether (−)-**3z**, derived from (−)-*N*,*N*-dicyclohexyl-(1*S*)-isoborneol-10-sulfonamide, only (−)-**6bz** and (+)-**8bz** were obtained (*endo/exo* = 85/15), reflecting a 100% de (4*R*) (Table 2). The totally asymmetric production of 4R diastereoisomers was also found in the cycloadditions of (−)-**3z** with **1a** and **1c** (Table 2) allowing (+)-**8az** and (−)-**6cz**, respectively, to be isolated in pure form. The adduct **6az** was the main reaction product of the cycloaddition of (−)-**3z** with **1a**, but it isomerized easily to (+)-**8az** during purification by recrystallization (see Experimental Section). The total asymmetric induction obtained using (−)-**3z** is a good omen for the subsequent objectives aimed at converting nitronate into highly enantiomerically enriched compounds.

The following absolute configurations of (+)-**6bx**, **7bx**, **8bx**, and **9bx** were assigned. The proton coupling constants (Table S1, see Supporting Information) and NOE experiments (see the discussion above for **4b** as an example) allowed the *cis* nitronates (+)-**6bx** and **7bx** to be recognized with respect to the *trans* ones **8bx** and **9bx**. The *cis* adduct (+)-**6bx** epimerizes to the *trans* **8bx** and the *cis* **7bx** to **9bx**. The X-ray analysis of (+)-**6bx** (Figure S1, see Supporting Information) allowed the configuration of stereogenic centers 4*R* and 6*S* to be assigned. The absolute configurations of the other three diastereoisomers were consequently assigned.

Similarly, the NMR data and X-ray analyses of (+)-**7by**, (+)-**8by**,[23] and (−)-**6bz** (Figures S2−S4, see Supporting Information) allowed the absolute configurations of four diastereoisomers [**6by**, (+)-**7by**, (+)-**8by**, and **9by**] to be assigned, as well as two epimers [(−)-**6bz** and (+)-**8bz**] produced by cycloadditions of **1b** with (+)-**3y** and (−)-**3z**, respectively. The *cis* and *trans* configurations of **6az**, (−)-**6cz** and (+)-**8az**, **8cz** were assigned by proton coupling constants (Table S1) and NOE experiments. The absolute configurations were assigned on the basis of structures of strictly analogous compounds (−)-**6bz** and (+)-**8bz**.

The facial selectivity of [4 + 2] cycloadditions of nitroalkenes **1** with optically active vinyl ethers **3** are dictated by the shape of the chiral auxiliary, as well as by the *s-cis* or *s-trans* reactive conformation of vinyl ether.[8,9]

Molecular calculations using the Hyperchem program on (+)-**3x** and (+)-**3y** suggest that the ground state conformation of both vinyl ethers is a pseudo-*s-trans* geometry with the C=CO−C dihedral angles Φ = −174.25° and −137.12°, respectively, in which the *re*-face [24] of the vinyl group is only moderately shielded with respect to the *si*-face (Figure 1, A and B). This is in agreement with the low facial selectivity (18 and 30% de (4*R*), Table 2) in favor of an *endo-unlike* combination of reagents: approach of the *si*-face of the vinyl ether to the *re*-face of the nitroalkene.

The facial selectivity of vinyl ether (−)-**3z**, in contrast, is total. Molecular calculations on (−)-**3z** suggest that the ground state conformation is a pseudo-*s-trans* geometry, Φ = −178.52°, in which one of the cyclohexyl ring systems effectively shields the *re*-face of the vinyl π-system (Figure 1, C), strongly favoring the *unlike* topicity (combination of *si*-face of vinyl ether with *re*-face of nitroalkene) in the *endo*-approach of the reagents. The *endo*-approach is favored by secondary orbital interactions $N^{\oplus}\cdots OR^*$ as already mentioned above.

In conclusion, a [4 + 2] cycloaddition of (*E*)-2-aryl-1-cyano-1-nitroalkenes **1** with achiral and enantiopure vinyl ethers **2** and **3** in pure water are highly *endo* selective, and by using (−)-*N*,*N*-dicyclohexyl-(1*S*)-iso-

(22) When the reaction mixture 60:30:5:5 [*endo/exo* = 90: 10, 30% de (4*R*)] of nitronates **6by**, (+)-**7by**, (+)-**8by**, and **9by** (Table 2) is maintained in DMSO for 30 min at room temperature, the ratio of components changes to 11:11:54:24 [*endo/exo* = 22:78, 30% de (4*R*)] showing that the epimerization rate of **6by** to (+)-**8by** is faster than that of (+)-**7by** to **9by**. The constancy of the de (4*R*) value, before and after the treatment of nitronate, supports the idea that an epimerization reaction occurs.

(23) The X-ray structure plot of (+)-**8by** (Figure S3, see Supporting Information) refers to crystal data of not refined structure (R = 19%); crystal system: orthorombic; space group: $P2(1)2(1)2(1)$; unit cell dimension a = 9.92 Å, b = 26.18 Å, c = 7.91 Å, $\alpha = \beta = \gamma = 90°$; V = 2056.9 Å^3; Z = 4; density (calculated) 1.24 mg/m^3. The low R value does not impugn the constitution and stereochemistry of compound.

(24) The *si* and *re* faces of vinyl ether are defined with respect to the C-alkoxy-bearing carbon atom.[8b] The *si* and *re* face of nitroalchene are defined with respect to the β-carbon.[9]

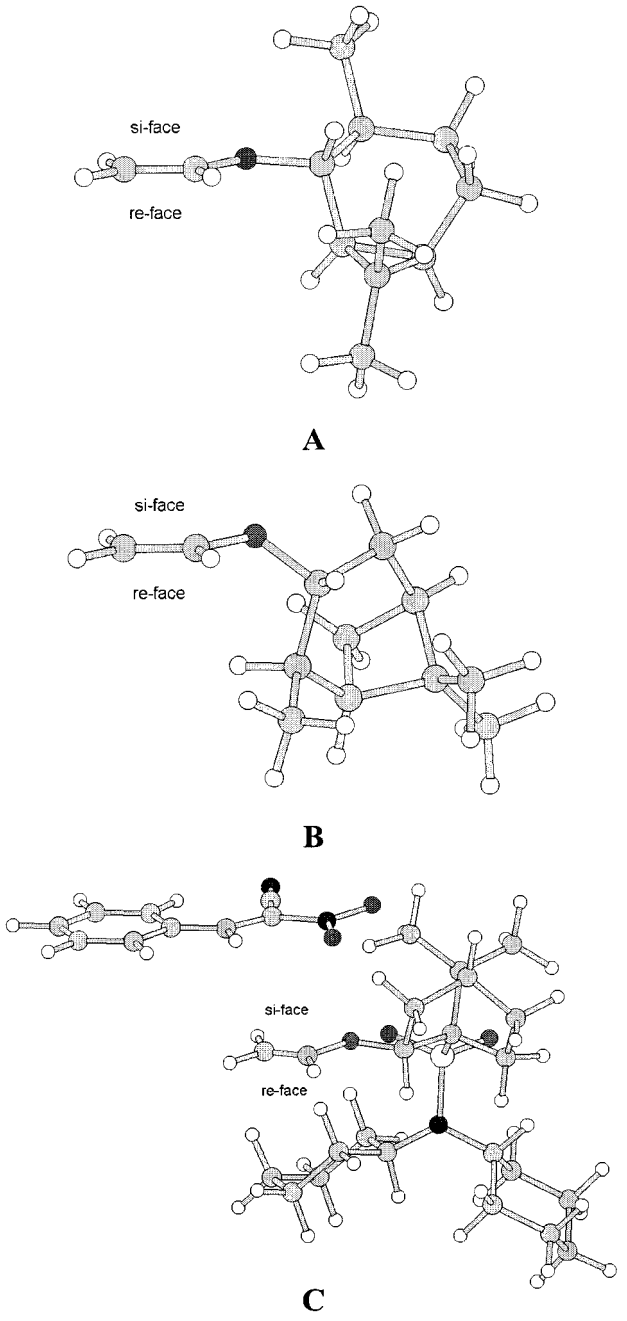


Figure 1. Lowest energy conformer of **A**: (+)-**3x** (Φ = −174.25°); **B**: (+)-**3y** (Φ = −137.12°); **C**: (−)-**3z** (Φ = −178.52°) with *endo*-mode, *si*-face (−)-**3z** - *re*-face **1**, approach.

borneol-10-sulfonamide as chiral auxiliary, totally asymmetric cycloadditions are observed.

This is the highest asymmetric induction value of [4 + 2] cycloaddition performed in sole water reported in the literature.

Although the reactions were carried out in heterogeneous conditions, they were fast and occurred quantitatively under mild conditions. Further studies on the conversion of optically pure nitronates into enantiomerically enriched compounds are in progress.

Experimental Section

Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or acetone-d_6 solutions on 200 and 400 MHz spectrometers. The X-ray data for compounds (+)-**6bx**, (+)-**7by**, and (+)-**8by**[23] were measured with a single-crystal diffractomer equipped with graphite-mono-chromatized Mo−Kα radiation (λ = 0.71069 Å); the X-ray data for compounds (−)-**6bz** were measured on an Xcalibur system, developed by Kuma diffraction Ltd equipped with a CCD detector and a 4-circle kappa geometry goniometer. The structures were solved by direct methods using the SIR97 program package[25] and refined by the full-matrix least-squares methods with SHELX93.[26] Column chromatography was carried out on silica gel (0.04−0.063 mm, 230−240 mesh ASTM) pretreated with 2.5% v/v of Et_3N and *n*-hexane as eluent. To avoid or reduce *the cis*−*trans* epimerization at C-6 of nitronates, the recrystallizations were carried out dissolving the product in the suitable solvent at room temperature and cooling at 0°/−20 °C.

(+)-2-Isocaranyl Vinyl Ether (3x). A mixture of (−)-2-isocaranol[27] (1.54 g, 0.01 mol), $Hg(OAc)_2$ (0.80 g, 0.025 mol), and *n*-butyl vinyl ether (85 mL) was stirred at 60 °C for 4.5 h. $Hg(OAc)_2$ (0.80 g, 0.025 mol) was again added and the mixture heated at 60 °C for 4.5 h. The mixture, cooled to 40 °C, was quenched with an aqueous saturated solution of K_2CO_3 and extracted with *tert*-butyl methyl ether. The organic phase was dried (Na_2SO_4), and after filtration and evaporation of the solvent under reduced pressure, the residue was purified by flash column chromatography to give 0.81 g of pure **3x** as oil (yield 45%).

$[\alpha]^{20}_D$ + 52.0 (*c* 1.24 $CHCl_3$); ^{1}H NMR 200 MHz ($CDCl_3$) δ: 0.66 (m, 2H); 0.80 (m, 1H) 0.93 (d, 3H, *J* = 6.2 Hz); 1.01 (s, 3H); 1.02 (s, 3H); 1.35−1.95 (m, 4H); 3.15 (db, 1H, *J* = 10.6 Hz); 4.01 (dd, 1H, *J* = 6.8, 1.3 Hz); 4.20 (dd, 1H, *J* = 14.4, 1.2 Hz); 6.4 (dd, 1H, *J* = 14.4, 6.8 Hz). ^{13}C NMR 50 MHz ($CDCl_3$) δ: 15.1, 16.5, 18.2, 19.0, 20.1, 27.4, 28.6, 30.1, 34.0, 78.7, 86.9, 150.6. Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.89; H, 11.21.

(+)-Isopinocampheyl Vinyl Ether (3y). A mixture of (+)-isopinocampheol (1.54 g, 0.01 mol), $Hg(OAc)_2$ (0.80 g, 0.025 mol), and *n*-butyl vinyl ether (85 mL) was stirred at 60 °C for 2.5 h. $Hg(OAc)_2$ (0.80 g, 0.025 mol) was again added and the mixture heated at 60 °C for 2.5 h. The mixture workup, as described for **3x**, affords after purification by flash column chromatography pure **3y** (0.86 g, 48%) as an oil.

$[\alpha]^{20}_D$ +71.3 (*c* 1.08 $CHCl_3$); ^{1}H NMR 200 MHz ($CDCl_3$) δ: 0.93 (s, 3H); 1.08 (d, 1H, *J* = 8.5 Hz), 1.12 (d, 3H, *J* = 7.4 Hz); 1.23 (s, 3H); 1.73−1.86 (m, 2H); 1.94 (m, 1H), 2.14 (m, 1H), 2.25−2.55 (m, 2H); 4.00 (dd, 1H, *J* = 6.7, 1.5 Hz); 4.10 (ddd, 1H, *J* = 8.9, 4.5, 4.5 Hz), 4.24 (dd, 1H, *J* = 14.2, 1.5 Hz); 6.36 (dd, 1H, *J* = 14.2, 6.7 Hz). ^{13}C NMR 50 MHz ($CDCl_3$) δ: 20.9, 23.7, 27.4, 33.1, 35.6, 38.3, 41.3, 44.2, 47.4, 78.7, 88.1, 151.2. Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.91; H, 11.17.

(1*S*)-(−)-10-(*N*,*N*-Dicyclohexylsulfonamide) Isoborneyl Vinyl Ether (3z). A mixture of (−)-*N*,*N*-dicyclohexyl-(1*S*)-isoborneol-10-sulfonamide (1.59 g, 0.004 mol), $Hg(OAc)_2$ (0.86 g, 0.0027 mol), and *n*-butyl vinyl ether (35 mL) was stirred at 120 °C for 15 h in a closed reactor. The mixture workup, as above-described for **3x** and **3y**, affords after purification by flash column chromatography pure **3z** (1.35 g, 80%) as a white solid.

mp 115−117 °C (*n*-hexane); $[\alpha]^{20}_D$ −17.11 (*c* 1.2 $CHCl_3$). ^{1}H NMR 200 MHz ($CDCl_3$) δ: 0.87 (s, 3H); 0.97 (s, 3H); 0.8−2.1 (m, 27 H), 2.65 (d, 1H, *J* = 13.3 Hz); 3.26 (m, 2H); 3.38 (d, 1H, *J* = 13.3 Hz); 3.95 (dd, 1H, *J* = 6.6, 1.4 Hz), 4.20 (dd, 1H, *J* = 14.1, 1.4 Hz); 4.20 (m, 1H); 6.33 (dd, 1H, *J* = 14.1, 6.6 Hz). ^{13}C NMR 50 MHz δ: 20.1, 20.4, 25.2 (2 C), 26.4 (4 C), 27.2, 29.2, 32.5 (2 C), 33.0 (2 C), 38.7, 44.5, 48.7, 50.2, 53.4, 57.2 (2 C), 83.2, 87.6, 151.1. Anal. Calcd for $C_{24}H_{41}NO_3S$: C, 68.04; H, 9.75; N, 3.31. Found: C, 68.22; H, 9.67; N, 3.35.

[4 + 2] Cycloadditions of Nitroalkenes 1 with Ethyl Vinyl Ether 2. A mixture of nitroalkene **1** (1 mmol) and ethyl

(25) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.

(26) Sheldrick, G. M., SHELXL 93, Program for the Refinement of Crystal Structures, University of Göttingen, 1993.

(27) Fringuelli, F.; Piermatti, O.; Pizzo, F.; Scappini, A. M. *Gazz. Chim. Ital.* **1995**, *125*, 195.

vinyl ether **2** (4 mmol for **1a** and **1b**; 8 mmol for **1c**) in pure water or in CH_2Cl_2 (5 mL) was stirred at the temperature and for the time reported in Table 1. Usual workup gave a mixture of **4** and **5** (see Table 1). Recrystallization allowed the pure cycloadducts **4** to be isolated. The yields are reported in Table 1.

***cis*-6-Ethoxy-4-phenyl-5,6-dihydro-4*H*-1,2-oxazine-3-carbonitrile 2-Oxide (4a).** mp 101−103 °C (diethyl ether); ^{1}H NMR 200 MHz (acetone-d_6) δ: 1.23 (t, 3H, J = 7.1 Hz); 2.18 (ddd, 1H, J = 14.0, 7.9, 5.1 Hz), 2.80 (ddd, 1H, J = 14.0, 8.1, 4.1 Hz); 3.77 (dq, 1H, J = 9.7, 7.1 Hz), 3.97 (dq, 1H, J = 9.7, 7.1 Hz); 4.25 (t, 1H, J = 8.0 Hz); 5.83 (dd, 1H, J = 5.1, 4.1 Hz); 7.30−7.50 (m, 5H). ^{13}C NMR 50 MHz (acetone-d_6) δ: 15.1, 34.9, 40.3, 66.6, 105.6, 106.2, 113.0, 128.8, 129.1 (2 C), 129.6 (2 C), 139.1. Anal. Calcd for $C_{13}H_{14}N_2O_3$: C, 63.40; H, 5.73; N, 11.38. Found: C, 63.42; H, 5.70; N, 11.42.

***cis*-4-(4-Chlorophenyl)-6-ethoxy-5,6-dihydro-4*H*-1,2-oxazine-3-carbonitrile 2-Oxide (4b).** mp 111−112 °C (diethyl ether); ^{1}H NMR 200 MHz (acetone-d_6) δ: 1.23 (t, 3H, J = 7.1 Hz); 2.19 (ddd, 1H, J = 14.0, 7.1, 4.6 Hz), 2.80 (ddd, 1H, J = 14.0, 8.2, 4.0 Hz); 3.77 (dq, 1H, J = 9.7, 7.1 Hz), 3.96 (dq, 1H, J = 9.7, 7.1 Hz); 4.30 (dd, 1H, J = 8.2, 7.1 Hz); 5.82 (dd, 1H, J = 4.6, 4.0 Hz); 7.40−7.50 (m, 4H).^{13}C NMR 50 MHz (Acetone-d_6) δ: 15.1, 34.5, 39.7, 66.7, 105.1, 106.2, 113.0, 129.7 (2 C), 131.1 (2 C), 134.3, 138.3. Anal. Calcd for $C_{13}H_{13}N_2O_3Cl$: C, 55.62; H, 4.67; N, 9.98. Found: C, 55.65; H, 4.64; N, 9.95.

***cis*-6-Ethoxy-4-(4-methoxyphenyl)-5,6-dihydro-4*H*-1,2-oxazine-3-carbonitrile 2-Oxide (4c).** mp 126−129 °C (*n*-hexane/ethyl acetate); ^{1}H NMR 200 MHz (acetone-d_6) δ: 1.24 (t, 3H, J = 7.1 Hz); 2.16 (ddd, 1H, J = 14.0, 7.9, 5.1 Hz), 2.78 (ddd, 1H, J = 14.0, 8.1, 4.2 Hz); 3.79 (dq, 1H, J = 9.8, 7.1 Hz), 3.81 (s, 3H); 3.98 (dq, 1H, J = 9.8, 7.1 Hz); 4.19 (t, 1H, J = 8.0 Hz); 5.82 (dd, 1H, J = 5.1, 4.2 Hz); 6.96 (m, 2H); 7.37 (m, 2H). Anal. Calcd for $C_{14}H_{16}N_2O_4$: C, 60.86; H, 5.84; N, 10.14. Found: C, 60.89; H, 5.82; N, 10.11.

[4 + 2] Cycloadditions of Nitroalkenes 1 with Enantiopure Vinyl Ethers 3. A mixture of nitroalkene **1** (1 mmol) and vinyl ether **3** (1.2 mmol) in pure water (5 mL) was stirred at the temperature and for the time reported in Table 2. Usual workup gave a mixture of nitronates **6**−**9** (see Table 2). Recrystallization allowed the pure cycloadducts to be isolated.

(4*R*,6*S*)-*cis*-4-(4-Chlorophenyl)-6-(2-isocaranoxy)-5,6-dihydro-4*H*-1,2-oxazine-3-carbonitrile 2-Oxide (6bx). Yield 82%; mp 145−146 °C (*n*-hexane/ethyl acetate); $[\alpha]^{20}_D$ +94.1 (*c* 0.55 $CHCl_3$). ^{1}H NMR 400 MHz (acetone-d_6) δ: 0.65−0.75 (m, 2H); 0.87 (m, 1H); 0.96 (d, 3H, J = 6.4 Hz); 0.99 (s, 3H); 1.01 (s, 3H); 1.35−1.85 (m, 4H); 2.25 (ddd, 1H, J = 14.1, 6.6, 4.4 Hz); 2.90 (ddd, 1H, J = 14.1, 8.7, 4.0 Hz); 3.33 (dd, 1H, J = 10.5, 2.7 Hz); 4.35 (dd, 1H, J = 8.7, 6.6 Hz), 6.01 (t, 1H, J = 4.2 Hz), 7.50 (m, 4H). ^{13}C NMR 50 MHz ($CDCl_3$) δ: 15.4, 17.2, 18.1, 18.3, 21.0, 26.7, 28.7, 30.3, 33.7, 34.4, 39.0, 79.6, 101.7, 104.0, 111.9, 129.3 (2 C), 129.7 (2 C), 134.4, 136.4. Anal. Calcd for $C_{21}H_{25}N_2O_3Cl$: C, 64.86; H, 6.48; N, 7.20. Found: C, 64.91; H, 6.42; N, 7.21.

(4*S*,6*R*)-*cis*-4-(4-Chlorophenyl)-6-(2-isopinocamphoxy)-5,6-dihydro-4*H*-1,2-oxazine-3-carbonitrile 2-Oxide (7by). Yield 80%; mp 126−128 °C (diethyl ether); $[\alpha]^{20}_D$ + 109.0 (*c* 0.22 $CHCl_3$). ^{1}H NMR 400 MHz (acetone-d_6) δ: 0.92 (s, 3H); 0.94 (d, 1H, J = 9.9 Hz); 1.16 (d, 3H, J = 7.4 Hz); 1.21 (s, 3H); 1.75 (m, 1H); 1.82 (m, 1H); 1.93 (m, 1H); 2.10 (m, 1H); 2.22 (ddd, 1H, J = 14.1, 6.4, 4.5 Hz); 2.37 (m, 1H); 2.57 (m, 1H); 2.83 (ddd, 1H, J = 14.1, 8.4, 3.9 Hz); 4.26 (ddd, 1H, J = 9.4, 4.6, 4.6 Hz); 4.34 (dd, 1H, J = 8.4, 6.4 Hz); 5.93 (t, 1H, J = 4.2 Hz); 7.48 (m, 4H). ^{13}C NMR 50 MHz ($CDCl_3$) δ: 20.1, 23.5, 27.1, 33.5, 34.7, 36.5, 38.0, 38.6, 41.0, 43.8, 47.0, 78.4, 102.4, 103.8, 112.0, 128.8 (2 C), 129.5 (2 C), 133.8, 136.5. Anal. Calcd for $C_{21}H_{25}N_2O_3Cl$: C, 64.86; H, 6.48; N, 7.20. Found: C, 64.92; H, 6.45; N, 7.22.

(4*R*,6*R*)-*trans*-4-(4-Chlorophenyl)-6-(2-isopinocamphoxy)-5,6-dihydro-4*H*-1,2-oxazine-3-carbonitrile 2-Oxide (8by). Yield 85%; mp 171−172 °C (*n*-hexane/ethyl acetate); $[\alpha]^{20}_D$ + 244.6 (*c* 0.56 $CHCl_3$). ^{1}H NMR 400 MHz (acetone-d_6) δ: 0.94 (s, 3H); 1.04 (d, 1H, J = 9.8 Hz); 1.11 (d, 3H, J = 7.4 Hz); 1.23 (s, 3H); 1.8−1.9 (m, 2H); 1.96 (m, 1H); 2.11 (m, 1H); 2.33 (ddd, 1H, J = 13.9, 11.8, 2.7 Hz); 2.40 (m, 1H); 2.49 (ddd, 1H, J = 13.9, 7.2, 2.1 Hz); 2.62 (m, 1H); 4.29 (ddd, 1H, J = 9.3, 4.9, 4.9 Hz); 4.40 (dd, 1H, J = 11.8, 7.2 Hz); 5.90 (t, 1H, J = 2.4 Hz); 7.50 (m, 4H). ^{13}C NMR 50 MHz ($CDCl_3$) δ: 20.3, 23.7, 27.4, 33.2, 33.8, 35.0, 38.2, 38.4, 41.3, 44.1, 47.3, 78.0, 101.4, 103.0, 112.0, 129.1 (2 C), 129.7 (2 C), 134.6, 135.8. Anal. Calcd for $C_{21}H_{25}N_2O_3Cl$: C, 64.86; H, 6.48; N, 7.20. Found: C, 64.89; H, 6.18; N, 7.20.

(4*R*,6*S*)-*cis*-6-[(1*S*)-10-(*N*,*N*-Dicyclohexylsulfonamide)-isoborneyl]-4-phenyl-5,6-dihydro-4*H*-1,2-oxazine-3-carbonitrile 2-Oxide (6az).[28] ^{1}H NMR 200 MHz (acetone-d_6) δ: 0.86 (s, 3H); 1.00 (s, 3H); 0.8−2.0 (m, 27H); 2.30 (ddd, 1H, J = 12.9, 7.8, 4.8 Hz); 2.71 (d, 1H, J = 13.4 Hz); 2.92 (ddd, 1H, J = 12.9, 7.8, 4.8 Hz); 3.23 (m, 2H); 3.26 (d, 1H, J = 13.4 Hz); 4.05 (dd, 1H, J = 7.8, 3.7 Hz); 4.29 (t, 1H, J = 8.1 Hz); 5.85 (t, 1H, J = 4.7 Hz); 7.30−7.55 (m, 5H). ^{13}C NMR 50 MHz ($CDCl_3$) δ: 20.1, 20.4, 25.0 (2 C), 26.3 (4 C), 26.9, 30.6, 32.4 (2 C), 33.0 (2 C), 35.4, 39.6, 40.1, 44.3, 48.7, 50.7, 53.9, 57.5 (2 C), 87.9, 104.9, 108.0, 111.9, 127.8 (2 C), 128.5, 129.2 (2 C), 137.3.

(4*R*,6*R*)-*trans*-6-[(1*S*)-10-(*N*,*N*-Dicyclohexylsulfonamide)-isoborneyl]-4-phenyl-5,6-dihydro-4*H*-1,2-oxazine-3-carbonitrile 2-Oxide (8az). Yield 85%; mp 170−171 °C (*n*-hexane/ethyl acetate); $[\alpha]^{20}_D$ +18.3 (*c* 0.75 $CHCl_3$). ^{1}H NMR 200 MHz (acetone-d_6) δ: 0.88 (s, 3H); 1.05 (s, 3H); 0.9−2.0 (m, 27H); 2.36 (ddd, 1H, J = 13.8, 11.6, 2.5 Hz); 2.50 (ddd, 1H, J = 13.8, 7.3, 2.3 Hz); 2.82 (d, 1H, J = 13.4 Hz); 3.30 (m, 2H); 3.42 (d, 1H, J = 13.4 Hz); 4.13 (dd, 1H, J = 6.6, 4.0 Hz); 4.29 (dd, 1H, J = 11.6, 7.3 Hz); 5.80 (t, 1H, J = 2.4 Hz); 7.3−7.5 (m, 5H). ^{13}C NMR 50 MHz ($CDCl_3$) δ: 20.1 (2 C), 25.0 (2 C), 26.4 (2 C), 26.5 (2 C), 26.9, 30.6, 32.6 (2 C), 32.9 (2 C), 32.8, 39.0, 40.1, 44.3, 48.9, 50.7, 54.0, 57.6 (2 C), 86.4, 103.3, 106.0, 112.0, 127.6 (2 C), 128.7, 129.4 (2 C), 137.1. Anal. Calcd for $C_{33}H_{47}N_3O_5S$: C, 66.30; H, 7.92; N, 7.03. Found: C, 66.35; H, 7.88; N, 7.00.

(4*R*,6*S*)-*cis*-4-(4-Chlorophenyl)-6-[(1*S*)-10-(*N*,*N*-dicyclohexylsulfonamide)isoborneyl]-5,6-dihydro-4*H*-1,2-oxazine-3-carbonitrile 2-Oxide (6bz). Yield 78%; mp 174−176 °C (diethyl ether); $[\alpha]^{20}_D$ −30.46 (*c* 0.86 $CHCl_3$). ^{1}H NMR 400 MHz (acetone-d_6) δ: 0.87 (s, 3H); 1.00 (s, 3H); 0.9−2.1 (m, 27H); 2.33 (ddd, 1H, J = 14.0, 7.4, 4.3 Hz); 2.73 (d, 1H, J = 13.5 Hz); 2.95 (ddd, 1H, J = 14.0, 8.3, 4.8 Hz); 3.24 (m, 2H); 3.26 (d, 1H, J = 13.5 Hz); 4.05 (dd, 1H, J = 8.0, 3.5 Hz); 4.35 (t, 1H, J = 7.8 Hz); 5.84 (t, 1H, J = 4.6 Hz); 7.51 (m, 4H). ^{13}C NMR 50 MHz ($CDCl_3$) δ: 20.0, 20.3, 24.9 (2 C) 26.2 (4 C), 26.8, 30.6, 32.3 (2 C), 32.9 (2 C), 34.7, 38.7, 40.0, 44.2, 48.6, 50.6, 53.8, 57.4 (2 C), 87.9, 104.0, 107.7, 111.8, 129.2 (4 C), 134.2, 136.1. Anal. Calcd for $C_{33}H_{46}N_3O_5SCl$: C, 62.69; H, 7.33; N, 6.65. Found: C, 62.75; H, 7.38; N, 6.57.

(4*R*,6*R*)-*trans*-4-(4-Chlorophenyl)-6-[(1*S*)-10-(*N*,*N*-dicyclohexylsulfonamide)isoborneyl]-5,6-dihydro-4*H*-1,2-oxazine-3-carbonitrile 2-Oxide (8bz). Yield 82%; mp 175−176 °C (*n*-hexane/ethyl acetate); $[\alpha]^{20}_D$ +30.36 (*c* 0.5 $CHCl_3$). ^{1}H NMR 400 MHz (acetone-d_6) δ: 0.88 (s, 3H); 1.04 (s, 3H); 0.9−2.0 (m, 27H); 2.41 (ddd, 1H, J = 13.9, 11.9, 2.6 Hz); 2.53 (ddd, 1H, J = 13.9, 7.1, 2.2 Hz); 2.77 (m, 1H, J = 13.4 Hz); 3.31 (m, 2H); 3.42 (m, 1H, J = 13.4 Hz); 4.13 (dd, 1H, J = 7.5, 3.8 Hz); 4.36 (dd, 1H, J = 11.9, 7.1 Hz); 5.81 (t, 1H, J = 2.3 Hz); 7.50 (m, 4H). ^{13}C NMR 50 MHz ($CDCl_3$) δ: 20.2 (2 C), 25.1 (2 C) 26.4 (2 C), 26.5 (2 C), 26.9, 30.6, 32.7 (2 C), 32.9 (2 C), 32.7, 38.6, 40.1, 44.3, 48.9, 50.8, 54.2, 57.7 (2 C), 86.5, 102.7, 105.9, 111.9, 129.0 (2 C), 129.7 (2 C), 134.7, 135.7. Anal. Calcd for $C_{33}H_{46}N_3O_5SCl$: C, 62.69; H, 7.33; N, 6.65. Found: C, 62.66; H, 7.31; N, 6.62.

(4*R*,6*S*)-*cis*-6-[(1*S*)-10-(*N*,*N*-Dicyclohexylsulfonamide)-isoborneyl]-4-(4-methoxyphenyl)-5,6-dihydro-4*H*-1,2-oxazine-3-carbonitrile 2-Oxide (6cz). Yield 80%; mp 174−176 °C (diethyl ether); $[\alpha]^{20}_D$ −34.1 (*c* 0.7 $CHCl_3$). ^{1}H NMR 200 MHz (acetone-d_6) δ: 0.88 (s, 3H); 1.03 (s, 3H); 0.8−2.0 (m, 27H); 2.29 (ddd, 1H, J = 13.9, 8.1, 4.6 Hz); 2.72 (d, 1H, J = 13.5 Hz); 2.92 (ddd, 1H, J = 13.9, 8.1, 4.9 Hz); 3.25 (m, 2H); 3.28 (d, 1H, J = 13.5 Hz); 3.79 (s, 3H) 4.04 (dd, 1H, J = 7.5, 3.5

(28) The epimerization of **6az** to **8az** which occurs during recrystallization prevents **6az** from being obtained in pure form, and the ^{1}H and ^{13}C NMR data refers to a **6az**:**8az** = 85:15 mixture.

Hz); 4.22 (t, 1H, J = 8.1 Hz); 5.83 (t, 1H, J = 4.8 Hz); 6.97 (dd, 2H, J = 6.7, 2.1 Hz); 7.41 (dd, 2H, J = 6.7, 2.1 Hz). Anal. Calcd for $C_{34}H_{49}N_3O_6S$: C, 65.04; H, 7.87; N, 6.69. Found: C, 65.13; H, 7.85; N, 6.65.

Acknowledgment. The Ministero dell'Università della Ricerca Scientifica (MURST) and the Consiglio Nazionale delle Ricerche (CNR-Roma) are thanked for financial support.

Supporting Information Available: ORTEP figures of **6bx**, **7by**, **8by**, and **6bz** (Figures S1−S4); tables of crystal data, atomic coordinates, bond lengths and angles, anisotropic thermal parameters, hydrogen coordinates, and torsion angles for compounds (+)-**6bx**, (+)-**7by**, and (−)-**6bz**; Table S1 of ^{1}H NMR data of nitronates **4**−**9** and ^{1}H and ^{13}C NMR peak assignment of compounds **3x**, **3y**, **3z**, **4a**, **4b**, **4c**, **6bx**, **7by**, **8by**, **6az**, **8az**, **6bz**, **8bz**, and **6cz**. This material is available free of charge via Internet at http://pub.acs.org.

JO010182V