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BENZENESULFONYLCARBONITRILE OXIDE. 5. FACE SELECTIVITY OF CYCLOADDITION TO CHIRAL TERMINAL ALKENES

Peter A. Wade*, Shankar M. Singh, and M. Krishna Pillay

Department of Chemistry, Drexel University,
Philadelphia, Pennsylvania 19104, U.S.A.

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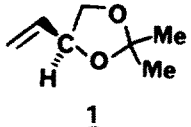
Abstract—The diastereomer ratio for cycloaddition of benzenesulfonylcarbonitrile oxide (BSNO) to a series of (S)-vinylglycine-derived alkenes varied from 30:70 to 66:34 depending on the substitutents at the chiral center. Isomer ratios were routinely determined by ^{1}H-NMR; isolation confirmed the results in several cases. Isomer assignment was based on comparison to acivicin where the absolute configuration has been determined by X-ray analysis. The results are interpreted as consistent with competitive cycloaddition to the alkene oriented in two differing conformations.

Nitrile oxide cycloadditions are rapidly becoming a standard tool for the synthesis of complex organic molecules. This is due in large part to the variety of synthetic transformations available for Δ^2-isoxazolines, the cycloadducts obtained from alkene dipolarophiles[1]. The possibility of employing chiral dipolarophiles to induce chirality at the 5- and/or 4-positions of isoxazolines therefore warrants systematic investigation. Several reports concerning the stereochemistry of nitrile oxide cycloadditions have already appeared, but these have centered on rigid systems (norbornylene[2]), cyclic systems (cyclopentenyl derivatives[3]), and intramolecular cases[4]. For simple terminal alkenes only the observation of moderate face selectivity for cycloaddition to the alkene 1 has been reported[5]. We have previously reported[6] no face selectivity for cycloaddition of BSNO (2) to the vicinally disubstituted double bond of *d*-limonene. Houk *et al.*[7] have conducted a theoretical study concerning the reactive conformation for cycloaddition to propene and application of the anti-periplanar effect[8] to nitrile oxide cycloadditions.



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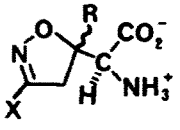
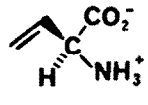


3a R = —H; X = Cl
b R = —H; X = SO_2Ph
c R = —H; X = Br

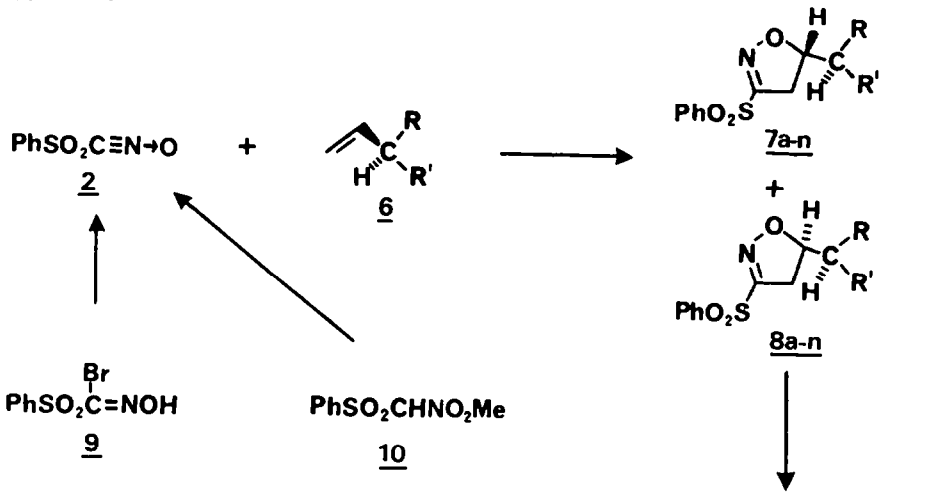
4a-c R = ···H



5a
b ·HCl

We report here our observations on face selectivity in nitrile oxide cycloadditions to chiral terminal alkenes. As part of a completed synthesis[9] of acivicin (3a) and its epimer 4a, the face selectivity was examined for reaction of BSNO (2) and a number of alkenes derived from (S)-vinylglycine hydrochloride (5b) (Scheme 1). It was felt that suitable modification of the amino and carboxyl groups of vinylglycine would permit considerable variation in face selectivity. It would then be possible to delineate the factors biasing attack on a particular face.

SCHEME 1.



a R = CO_2H; R' = $NHCO_2C(Me)_3$
b R = CO_2H; R' = $NHCO_2C(Et)_3$
c R = CO_2H; R' = $NHCO_2CH_2$(9-anthryl)
d R = CO_2H; R' = $NHCO_2CH_2$-[3,5-$(NO_2)_2C_6H_3$]
e R = CO_2H; R' = NHCO-[3,5-$(NO_2)_2C_6H_3$]
f R = CO_2H; R' = NHCOMe
g R = CO_2H; R' = N-[2-(NO_2)Pht]
h R = CO_2H; R' = NPht
i R = CO_2H; R' = NHCbz
j R = CO_2Me; R' = NHCbz
k R = CO_2Me; R' = NPht
l R = CH_2OH; R' = NHCbz
m R = CH_2OAc; R' = NHCbz
n R = $C(Me)_2OH$; R' = NHCbz

RESULTS

The 1,3-dipole BSNO cycloadded readily to all terminal alkenes which were investigated (Scheme 1). A total of fourteen different alkenes were examined in varying degrees of completeness (compounds 6a-n; Table 1). The yield of cycloadducts 7-8 ranged from 24-83% and was not optimized except for the N-phthalyl derivatives. The general reaction conditions involved slow addition of excess (1.5 - 3.2 equivalents) bromo oxime 9 to a stirred warmed mixture of dipolarophile, ground silver nitrate and THF. In one case (dipolarophile 6j) BSNO was generated from both 9 and nitronic ester 10[6]. Isomer ratios were routinely determined by integration of ^{1}H-NMR spectra; their accuracy is estimated at ±5%.

The dipolarophiles examined break down conveniently into four groups. The first group includes the carbamates 6a-d,i which were all prepared from (S)-vinylglycine (5a)[10] by treatment with the appropriate acylating agent, in most cases a *p*-nitrophenyl carbonate ester. The carbamate 6j[10], a precursor to 5, was also examined. Preferential cycloaddition on the (re, re)-face of the carbamate dipolarophiles to form the (5R, αS)-cycloadducts 8 occurred, although the preference was never large. For the *t*-butyl and 3,5-dinitrophenyl carbamates 6a and 6d, face selectivity was highest (30:70). The triethylmethyl carbamate 6b and the 9-anthrylmethyl carbamate 6c exhibited modest selectivity (40:60 isomer ratio). For the N-carbobenzoxy derivative 6i and its methyl ester 6j, face selectivity was lowest (45:55). The ratio for cycloaddition was not substantially altered by a 45° change in temperature. Generation of BSNO at 0-5°C (from nitronic ester 10[6]) or at 45-50°C

TABLE 1. DIASTEREOMER RATIOS FOR CYCLOADDITION.

DIPOLAROPHILE[a]	TEMPERATURE	CYCLOADDUCTS	YIELD, %	RATIO[b]
6a	40-45	7a, 8a	24	30:70
6b	40-45	7b, 8b	46[c]	40:60
6c	40-45	7c, 8c	72[c]	40:60[d]
6d	35-40	7d, 8d	64[c]	30:70
6e	40-45	7e, 8e	66[c]	40:60
6f	40-45	7f, 8f	41	38:62[e]
6g	40-45	7g, 8g	27[c]	40:60
6h	45-50 0-5	7h, 8h	80 25	38:62[e] 40:60
6i	45-50	7i, 8i	73[c]	45:55
6j	45-50 0-5[f]	7j, 8j	83 30	45:55 40:60
6k	20-25	7k, 8k	47	40:60
6l	40-45	7l, 8l	57	53:47[e]
6m	40-45	7m, 8m	77	50:50
6n	40-45	7n, 8n	46	66:34[e]

[a] BSNO was generated from bromooxime 9, unless otherwise stated. [b] Ratios are based on NMR, unless otherwise stated. [c] Yield is based on the methyl ester mixture. [d] Determined after removal of the 9-anthrylmethyl group. [e] Determined by isolation. [f] BSNO was generated from nitronic ester 10.

(from bromo oxime 9) gave only a 5% difference for cycloaddition to 6j (40:60 and 45:55 ratios, respectively). It is noteworthy that the slight increase in face selectivity at lower temperature was accompanied by a marked decrease in cycloadduct yield (30% and 83%, respectively).

The crude cycloadducts 7a-d,i and 8a-d,i were not separated; instead they were methylated with diazomethane. The mixture of esters 11 and 12 was purified by preparative-TLC and the integrated NMR signals for the carbomethoxy groups used to assign the diastereomer ratio. For 7c and 8c it was necessary to deprotect the nitrogen prior to obtaining an accurate integration. The assignment of the major diastereomers as 8a and 8c was made by deprotection of the nitrogen and NMR analysis of the mixture of amino acids 3b[1d] and 4b, available as pure materials from an alternate route. The NMR spectra of diastereomers 3b and 4b differ substantially; the α-proton of 3b is downfield (δ 3.86 vs. δ 3.69) and has the smaller coupling constant (2.7 Hz vs. 7.7 Hz) (Table 2). A similar situation has been noted for acivicin (3a) and its epimer 4a[11] as well as the 3-bromo analogs 3c and 4c[12]; the (5S, αS)-isomer has the more downfield α-proton and the smaller coupling constant (3 Hz) in both these cases. The relative order of TLC elutions are similar in that the (5R, αS)-isomers 4a-c all have the larger R_f ($BuOH-H_2O-AcOH$, 60:25:15). Assignment of the (5S,αS)-configuration to 3a rests on an X-ray determination[13]. Assignment of the major isomers as 8j, 12b and 12d was made by comparison of the relative carbomethoxy methyl absorptions to cycloadducts 12a and 12c. In all cases, the more downfield chemical shift was exhibited by the major isomer. Variation of the carbamate functionality would not be expected to

alter the relative chemical shifts for the two diastereomeric products. Indeed, the major isomer for each carbamate had a more upfield signal for the ring methylene and a more downfield signal for the methine.

The second set of dipolarophiles investigated were the amides 6e-f. These were readily preparable by acylation of 5a under standard conditions. Cycloaddition of BSNO gave isomer ratios of roughly 40:60 as determined by NMR. Th major cycloadduct was again assigned as the (5R αS)-isomer based on comparison of the methylate cycloadducts 11 and 12. Preparative TLC (chloro form-acetic acid, 96:4) separated 11f and 12 (38:62 weight ratio); similarly, 11e and 12e coul be separated by repetitive preparative TL (CH_2Cl_2-methanol, 99:01). Similar to the carbamates, the major stereoisomers 12e,f had th

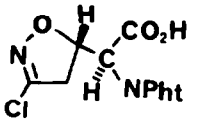
TABLE 2. NMR DATA FOR SEPARATED DIASTEREOMERS.

SPECIES	SOLVENT	^{1}H-NMR SPECTRUM (δ VALUES)[a]
3b[b]	D_2O	7.3-7.9 (m, 5H), 5.20 (m, 1H), 3.86 (d, 1H, J = 2.7 Hz), 3.43 (d, 2H, J = 10 Hz).
4b[b]	D_2O	7.3-7.9 (m, 5H), 5.10 (m, 1H), 3.69 (d, 1H, J = 7.7 Hz), 3.43 (d, 2H, J = 11 Hz).
11e	$CDCl_3$	9.16 (t, 1H, J = 1.9 Hz), 8.96 (d, 1H, J = 1.9 Hz), 7.5-8.1 (m, 6H), 5.30 (m, 1H), 4.95 (dd, 1H, J = 2.4, 7.6 Hz), 3.76 (s) on 3.5-3.9 (m, 2H) [total 5H].
12e	$CDCl_3$	9.10 (t, 1H, J = 2.0 Hz), 8.88 (d, 1H, J = 2.0 Hz), 7.3-8.0 (m, 6H), 5.55 (m, 1H), 5.17 (dd[c], 1H, J = 2.2, 8.8 Hz), 3.85 (s, 3H), 3.42-3.55 (m, 2H).
11f	$CDCl_3$	7.5-8.1 (m, 5H), 6.53 (br d, J = 7.8 Hz), 5.11 (m, 1H), 4.74 (dd, 1H, J = 2.6, 7.8 Hz), 3.70 (s) on 3.3-3.9 (m) [total 5H] and 2.04 (s, 3H).
12f	$CDCl_3$	7.5-8.1 (m, 5H), 6.21 (br d, J = 8.8 Hz), 5.40 (m, 1H), 4.92 (dd, 1H, J = 2.0, 8.8 Hz), 3.78 (s, 3H), 3.36 (m, 2H), 1.90 (s, 3H).
8j	$CDCL_3$	7.4-8.0 (m, 5H), 7.37 (s, 5H), 5.10 (s) on 5.0-5.6 (m) [4H total], 4.5-4.7 (m, 1H), 3.77 (S, 3H), 3.4-3.55 (m, 2H).
7k	C_3D_6O	7.91 (s) on 7.5-8.1 (m) [total 9H], 5.7 (m, 1H), 5.27 (d, 1H, J = 5.7 Hz), 3.68 (m, 2H).
8k	C_3D_6O	7.92 (s) on 7.6-8.1 (m) [total 9H], 5.62 (q, 1H, J = 8.8 Hz), 5.21 (d, 1H, J = 8.8 Hz), 3.75 (m, 2H).
7l[d]	$CDCl_3$	7.3-8.0 (m, 10H), 5.48 (d, J = 8.8 Hz), 5.08 Hz (s, 2H), 4.92 (m, 1H), 3.6-3.85 (m, 3H), 3.36 (m, 2H) and 2.25 (s, 1H)
8l[d]	$CDCl_3$	7.3-8.0 (m, 10H), 5.0-5.2 (m, 4H), 3.91 (m, 1H), 3.70 (m, 2H), 3.32 (m, 2H) and 2.26 (s, 1H).
7n	$CDCl_3$	7.5-8.0 (m, 5H), 7.34 (s, 5H), 5.10 (s) on 4.9-5.5 (m) [4H total], 3.85 (dd, 1H, J = 6.6, 7.8 Hz), 3.35 (d, 2H, J = 11.0 Hz), 1.29 and 1.22 (2s, 6H).
8n	$CDCl_3$	7.5-7.9 (m, 5H), 7.37 (s, 5H), 5.31 (m, 2H), 5.09 (s, 2H), 3.72 (d, 1H, J = 10 Hz), 3.38 (m, 2H), 2.0 (s, 1H), 1.35 (s, 3H) and 1.19 (s, 3H).
13	C_3D_6O	7.94 (s, 4H), 5.5 (m, 1H), 5.3 (d, 1H, J = 10.7 Hz), 3.57 (d, 2H, J = 10 Hz).
14	C_3D_6O	7.94 (s, 4H), 5.4 (m, 1H), 5.23 (d, 1H, J = 9.6 Hz), 3.67 (m, 2H).

[a] At 90 MHz relative to internal TMS unless otherwise stated. [b] Relative to external TMS-$CDCl_3$. [c] Saturation of the δ 5.55 signal [ring CH] gave δ 5.17 (d, J = 8.8 Hz). [d] At 250 MHz.

more downfield methyl absorption. Also similar to the carbamates, the major isomers had the more upfield ring methylene and the more downfield methine absorption. On the other hand, analysis of (5H, αH)-coupling constants and comparison to acivicin suggested that the major products were the (5S, αS)-isomers; the major isomers had the smaller coupling constant (2.0 and 2.2 Hz, respectively, vs. 2.4 and 2.6 Hz for the minor isomers). The (5S, αS)-assignment was eventually confirmed by methylation and acetylation of isoxazoline 4b to produce 12e.

The third group of dipolarophiles to be examined were the phthalimides 6g,h,k. These were prepared from 5a by standard phthalylation procedures[14] followed in the case of 6k by methylation with diazomethane. The cycloaddition ratios for 6h and 6k ranged from 40:60 to 35:65 in all cases. No discernible variation was noted from 0-45°C for alkene 6h. Preliminary attempts to induce association between the nitrile oxide and the carboxylic acid group of alkene 6h as a carboxylate salt did not alter the isomer ratio. Alkene 6h gave similar results as the magnesium salt and in the presence of



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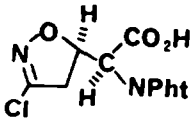

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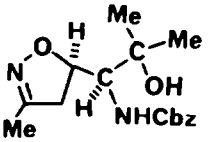
dichloroethylaluminum or boron trifluoride etherate. The isomer ratios for 7h,k and 8h,k were again determined by NMR spectra on the purified mixture of the methyl esters. Here the methyl absorptions were exactly coincident for the diastereomers, but the ring methyne of the major isomer was the more upfield and had the greater (5H, αH)-coupling constant (9.2 Hz vs. 6.0 Hz). Prelimimary examination of alkene 6g and the spectra of the methylated cycloadducts 11g and 12g led to similar results (40:60 isomer ratio). The cycloadducts 7h and 8h were separated by medium pressure liquid chromatography (38:62 weight ratio, respectively; benzene-acetic acid, 88:12). Removal of the phthalyl protecting group from 7h with hydrazine gave 3b; similarly, 8h gave 4b. Interestingly, cyanogen chloride N-oxide cycloadded with a slightly higher selectivity (30:70 weight ratio) as determined by separation of the N-phthalyl derivatives 13 and 14. Deprotection of 13 gave authentic[15] acivicin (3a) while 14 gave epimer 4a.

The fourth set of dipolarophiles to be investigated were the alcohol derivatives 6l-n. Alcohol 6l was conveniently obtained by LAH-reduction of (S)-vinylglycine (5a) followed by treatment with carbobenzoxy chloride, although the overall yield was only 16%. Acetylation of alcohol 6l gave acetate 6m in 90% yield. The alcohol 6n was obtained by reaction of (S)-vinylglycine precursor 6j with methyllithium (34% yield). Cycloaddition of BSNO on alcohol 6l gave a nearly equal mixture of the two diastereomers (55:45 ratio) which could be conveniently separated by chromatography (anhydrous ether, 53:47 weight ratio). We have tentatively assigned the major isomer as 7l based on analogy to the other carbobenzoxy derivatives 7i and 7j. The major cycloadduct has the more upfield ring methyne absorption. The amide hydrogen is downfield from the minor isomer again as in 7i, 7j. The acetate 6m gave approximately a 50:50 isomer ratio of cycloadducts based on the relative intensities of the methyl groups, which were too



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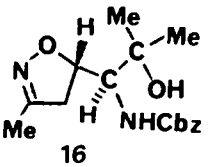

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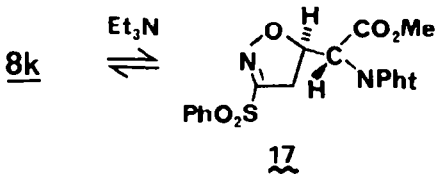
close to accurately integrate at 250 MHz. Indeed, all the absorptions for 7m and 7n overlapped at 250 MHz nor could the isomers be separated by thin layer chromatography. Cycloadduct 8l was converted to 8m by acetylation; 8m had the more downfield methyl absorption. Alcohol 6n gave a 46% yield of cycloadducts 7n and 8n which could be separated (anhydrous ether, 66:34 weight ratio). The (5R, αS)-isomer was assigned as the minor cycloadduct by conversion (methyllithium, -78°C, 57% yield) to the 3-methyl isoxazoline 15 and independent synthesis of the same compound from amino acid 4b. Compound 4b was treated with carbobenzoxy chloride (34% yield), diazomethane (36% yield) and methyllithium (14% yield) giving 15 free of the (5S, αS)-isomer 16. Treatment of the major cycloadduct 7n with methyllithium gave a 39% yield of the 3-methyl isoxazoline 16, clearly isomeric with 15.

The possibility of epimerizing the α-center of acivicin derivatives has been examined. Pure phthalimide 8h was methylated with diazomethane to provide the (5R, αS)-isomer 8k. Triethylamine treatment (refluxing methylene chloride) gave at equilibrium a 70:30 mixture of (5R, αS)- and (5R, αR)-isomers 8k and 17, respectively. The isomer ratio was determined by integration of the ring methines of the mixture.



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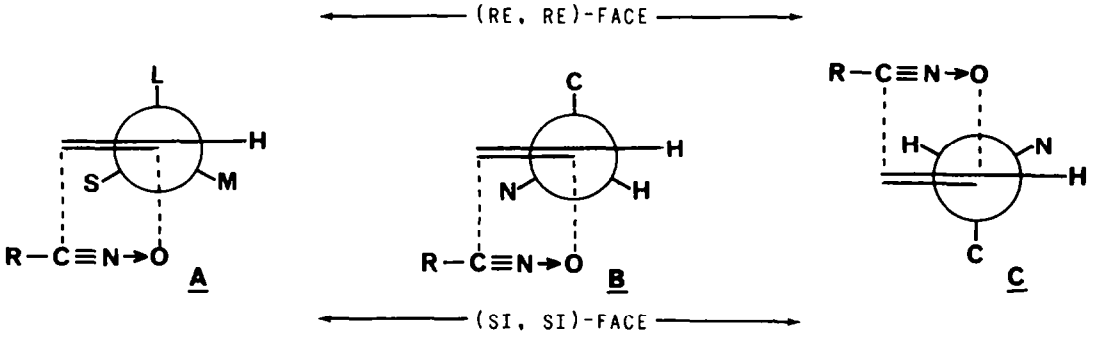
A short synthesis of acivicin has been developed from the model studies presented here[9]. Cycloaddition of cyanogen chloride N-oxide to phthalimide dipolarophile 6h gave a 52% yield (30:70 ratio) of the cycloadducts 13 and 14. Deprotection of cycloadduct 13 with hydrazine gave a 72% yield of acivicin (3a), identical (NMR, TLC and specific rotation) with an authentic sample.

DISCUSSION

Relatively poor stereoselectivity was exhibited by BSNO in cycloaddition to the chiral alkenes examined here. Since cycloadditions are highly sensitive to steric factors, this was not anticipated. However, the poor selectivity would be consistent with theory if the following facts are taken into consideration. First, nitrile oxides are linear; rather less steric interaction can be expected in the nitrile oxide cycloaddition transition state compared to Diels-Alder or nitrone transition states. Second, the C-C bond is further developed than the C-O bond so that the alkene chiral substitutuent should intereact less with the developing C-O bond than might otherwise be the case. Third, while reaction might be expected to proceed through the Felkin type transition state A[8b, 16] (L = large; M = medium; S = small), other possible conformational arrays at the allylic C-C bond might well compete in a mobile open-chain system.

A general feature noted here is that as the carbon substituent at the chiral center increased in size, attack ocurred more predominantly on the (si, si)-face. The trigonal carboxyl and carbomethoxy groups gave rise to preferential attack on the (re, re)-face (from 30:70 to 45:55 ratios) while the tetrahedral hydroxymethyl and acetoxymethyl functionalities of 6l and 6m directed attack about equally to either face. Dipolarophile 6n with a very large (dimethyl)hydroxymethyl group gave rise to preferential attack on the (si, si)-face (66:34 ratio). As the N-substituent at the chiral center went from mono- to diacyl, the preference for attack on the (re, re)-face increased somewhat (dipolarophiles 6h,k compared to 6i,j). This is precisely opposite to predictions based solely on transition state A. Increasing the bulk of the C-functionality should decrease attack on the (si, si)-face rather than increase the attack[8b, 16]. Also difficult to explain in terms of transition state A is the relatively large change in ratio encountered when the carbamate is changed from phenyl (6i, 45:55) to *t*-butyl (6a, 30:70). The group changed is five bonds from the prochiral center but has a greater influence than most group changes only two bonds from the prochiral center. One explanation for these results is that competing attack occurs through transition states B and C[17] (N = N-substituent; C = C-substituent; transition state



C is the mirror image of A when the C-substituent is largest). Lowest energy conformations for alkenes have the double bond eclipsed (or nearly so) with a substituent. Usually the preferred eclipsed substituent is H although heteroatoms (F^{16}, O^{17}, and possibly N^{18}) can also be eclipsed. The reacting transition states B and C reflect the prevailing anticipated low energy conformations for the alkene, but allow the developing C-O bond to be staggered. As was observed, a bulky C-substituent should favor attack on the (si, si)-face through transition state B. The bulky C-substituent should be repelled by the olefinic carbon to a greater extent forcing the N-substituent closer to the oxygen of the incoming nitrile oxide in transition state C. Transition state B would then be favored and attack would occur preferentilly on the (si, si)-face. When the C-substituent is less bulky, less interaction of the N-substituent of transition state C occurs favoring attack on the (re, re)-face. As the N-functionality increases in size, transition state C would again be favored.

There is no evidence for H-bonding as a major controlling influence in the present study. The dipolarophile acids 6h,i and the corresponding esters 6j,k gave similar isomer ratios. The dipolarophile alcohol 6l gave at most a 5% change in isomer ratio compared to the acetate 6m. However, H-bonding has been suggested as a controlling interaction in nitrile oxide cycloaddition to a cyclopentenyl dipolarophile[3]. Perhaps the high electrophilicity of BSNO precluded extensive H-bonding here. Also, the C-substituent in both transition states B and C would be anti to the incoming nitrile oxide oxygen and thus the hydroxyl and carboxyl groups would be incorrectly oriented for H-bonding to occur.

We have observed no strong evidence of controlling electronic factors other than a preference for the allylic-N to be near the C=C bond (transition state B). The nitrile oxide does not attack anti to the N-substituent although similar avoidance of O-substituents has been postulated in other cycloadditions[18], including nitrile oxide cycloaddition to dipolarophile 1[4b]. The dipolarophile acid 6i and alcohol 6l cycloadded with similar ratios (45:55 vs. 53:47) although the carboxyl group is clearly more electron-attracting than the hydroxymethyl group. On the other hand, the 3,5-dinitrophenyl carbamate 6e (30:70 ratio) did show a moderate preference compared to 6i (45:55 ratio). Complexation of the 3,5-dinitrophenyl group to the C=C double bond could lower attack on 6e through transition state B thus favoring attack on the (re, re)-face. Perhaps more likely is association of the 3,5-dinitrophenyl group with the allylic nitrogen increasing its bulk, again disfavoring attack through transition state B.

In summary, we conclude that stereochemical control is relatively limited for intermolecular nitrile oxide cycloadditions on chiral terminal alkenes. In this study we did not surpass a 3:1 preference, despite considerable variation in the nature of the chiral center substituents.

EXPERIMENTAL

General Methods. ^{1}H-NMR spectra were taken at 90 MHz on a JEOL FX-90Q instrument unless otherwise stated. Thin-layer chromatography was carried out on Analtech 0.25-mm silica gel GF analytical plates or 1.00-mm silica gel preparative plates. Reactions were typically run under N_2. Routine extractions were performed with CH_2Cl_2; organic layers were washed with water and dried over anhydrous sodium sulfate. Solutions were concentrated at reduced pressure.

(S)-vinylglycine hydrochloride (5b). Prepared by modification of a published procedure[10]. Crude methyl (S)-2-[[(benzyloxy)carbonyl]amino]-4-(methylsulfinyl)butanoate (25 g; 0.08 mol) was pyrolysed over a 12h period at 145-150°C (0.025 mm). The pyrolysate (12.8 g) was column chromatographed on silica gel; after elution with CH_2Cl_2 to remove sulfur-containing by-products, elution with CH_2Cl_2-ethyl acetate, 95:5 afforded 7.58 g (38% yield) of slightly impure (96% purity, TLC and NMR) 6j. Compound 6j was added to 6N hydrochloric acid (175 mL) and the mixture refluxed for 1h. The resulting solution was cooled, washed with chloroform and concentrated. The residue was triturated with hot acetone to afford 2.59 g (24% overall yield) of white 5b: mp 176-77°C (dec) [lit[10] 175-77°C]; $[\alpha]_D^{20}$ +83.5° (c 1.9, water) [lit[10] $[\alpha]_D^{20}$ +78.5°].

Preparation of 3,5-Dinitrobenzyl p-Nitrophenyl Carbonate (18a) and 1-(1,1-Diethyl)propyl p-Nitrophenyl Carbonate (18b). A general procedure[20] for 9-anthrylmethyl p-nitrophenyl carbonate (18c) was employed.

(S)-N-[[1-(1,1-Diethyl)propyl]oxycarbonyl]vinylglycine (6b). A mixture of 5b (0.21 g, 1.52 mMol), sodium carbonate (0.56 g) and DMSO (3 mL) was stirred while a solution of carbonate 18b (0.81 g; 3.04 mMol) in DMSO (3 mL) was added dropwise over 1h. After 16h stirring, the reaction mixture was added to water containing NaH_2PO_4 (1 g) (pH 6-7). Washing with ether and CH_2Cl_2 removed p-nitrophenol. Acidification with 2N HCl, extraction, concentration of the

organic layer and purification by preparative TLC (CH_2Cl_2-acetic acid, 97:3) gave 0.13 g (37% yield) of 6b as an oil: NMR ($CDCl_3$) δ 5.8-6.4 (m, 1H), 5.1-5.6 (m, 2H), 4.6-5.0 (m, 1H), 1.75 (q, 6H, J = 7 Hz), 0.81 (t, 9H, J = 7 Hz).

(S)-N-[(3,5-Dinitrobenzyl)oxycarbonyl]vinylglycine (6c). Prepared similar to 6b in 42% yield from the carbonate 18c. DMF was used as the solvent and was removed in vacuo prior to aqueous work-up: NMR ($CDCl_3$) δ 10.67 (s, 1H), 8.97 (t, 1H, J = 2.0 Hz), 8.55 (d, 1H, J = 2.0 Hz), 6.5-6.7 (broad m, 1H), 5.35 (S) on 5.2-6.2 (m, 5H), and 4.8-5.1 (m, 1H).

(S)-N-[(9-Anthrylmethyl)oxycarbonyl]vinylglycine (6d). Prepared similar to 6b. The crude product from reaction of 5b and 18a in DMSO was isolated by acidification (2N HCl), extraction, and concentration. Recrystallization from CH_2Cl_2-benzene-hexane gave a 67% yield of pure 6d: mp 201-204°C (dec); IR (KBr) 3320 (NH), 2500-3600 (COOH), 1670 cm^{-1} (br, C=O); NMR ($CDCl_3$) δ 7.5-8.7 (m, 9H), 6.17 (s, 2H) 5.2-6.2 (m, 4H), and 4.9-5.1 (m, 1H).

(S)-[N-(Benzyloxy)carbonyl]vinylglycine (6i). A solution of 5b (68 mg; 0.5 mMol) in 0.1N NaOH (10 mL) was treated alternately over 20 min with benzyl chloroformate (three portions; 94 mg total) and 0.1N NaOH (two portions; 7 mL total). After 15 min stirring, more base (3 mL 0.1N NaOH) was added and the solution washed with CH_2Cl_2. Acidification (2N HCl), addition of salt, extraction, concentration and preparative TLC gave 87 mg (74% yield) of pure 6i: IR (KBr) 3400 (NH), 2500-3600 (br, COOH), 1730 (C=O), and 1670 cm^{-1} (NHCO); NMR ($CDCl_3$) δ 7.38 (s, 5H), 5.9-6.3 (m, 1H), 5.1-5.6 (m, 2H), 5.07 (s, 2H), 4.8-5.0 (m, 1H).

Methyl (S)-(N-phthalyl)vinylglycine (6k). A cold (0-5°C) CH_2Cl_2 solution of acid 6h was treated with excess etheral CH_2N_2. The volatiles were stripped and a quantitative yield of ester 6j was obtained: mp 78-80°C; IR 1710 cm^{-1} (br, C=O); NMR ($CDCl_3$) δ 7.5-7.8 (m, 4H), 6.37 (ddd, 1H, J = 7, 9, 17 Hz), 5.1-5.45 (m, 3H), 3.75 (s, 3H).

When treated with triethylamine, compound 6k rapidly isomerized to the conjugated ester (NMR, TLC).

(S)-[N-3,5-Dinitrobenzoyl]vinylglycine (6e). Prepared from 5b (70 mg, 0.51 mMol) and 3,5-dinitrobenzoylchloride (243 mg, 1.05 mMol) similar to carbamate 6i. The crude product was purified by preparative TLC (CH_2Cl_2-acetic acid, 97:3) to give 121 mg (81% yield) of pure 6e: mp 161-63°C; IR (KBr) 3300 (NH), 2500-3600 (COOH), 1720 (C=O), 1640 (NHCO), 1530, and 1340 cm^{-1} (NO_2); NMR ($CDCl_3$) δ 9.14 and 9.05 (2s, 3H), 7.7-8.1 (broad m, 1H), 5.3-6.3 (m, 4H).

(S)-[N-acetyl]vinylglycine (6f). Prepared in 51% yield from (S)-vinylglycine (5a[10]) by a procedure[21] developed for the racemic modification: mp 155-57°C; IR (KBr) 3250 (NH), 2700-3700 (br, OH), and 1710 cm^{-1} (C=O); NMR (D_2O) 5.98 (ddd, 1H, J = 17.3, 9.7, 5.9 Hz), 5.2-5.5 (m, 2H), 4.88 (m, 1H), and 2.03 (s, 3H).

Cycloaddition. General. Nitrile oxide 2 was generated from bromo oxime 9 using excess silver nitrate (2 equivalents). The limiting reagent was the dipolarophile with 2 always in excess (1.5-3.3 equivalents). For dipolarophiles 6d, 6e, and 6k CH_2Cl_2 was used as solvent; for all others THF was routinely used as solvent. When the isomer ratio was determined for the methyl esters, excess diazomethane was added directly to the crude product. Two illustrative procedures are shown below.

Preparation and Methylation of 7d and 8d. A solution of 9 (0.2 g; 0.76 mMol) in CH_2Cl_2 (2 mL) was added dropwise over 1h (syringe pump technique) to a heated (35-40°C) mixture of dipolarophile 6d (78 mg; 0.24 mMol), silver nitrate (0.26 g; 1.52 mMol) and CH_2Cl_2 (2 mL). Additional CH_2Cl_2 (1 mL) was used to complete the transfer. The mixture was stirred 15 min at 35-40°C, cooled, and filtered. The silver salts were washed (CH_2Cl_2) and the filtrate combined with the washings. This solution, containing a crude mixture of 7d and 8d, was treated with excess etheral diazomethane. The solution was then concentrated and the product purified by preparative TLC (99:1, CH_2Cl_2). No TLC separation of 10d and 11d could be effected; 80 mg (64% yield) of the mixture was obtained.

Preparation and Separation of 7n and 8n. To a heated (40-45°C) mixture of dipolarophile 6n (33 mg; 0.13 mMol), silver nitrate (89 mg) and THF (0.5 mL) was added dropwise over 1h (syringe pump technique) a solution of 9 (70 mg; 0.26 mMol) in THF (0.6 mL). Additional THF (0.5 mL) was used to complete the transfer. The mixture was stirred 15 min at 40-45°C, cooled, and filtered. The silver salts were washed (CH_2Cl_2) and the combined filtrate and washings concentrated. The crude product was purified by preparative TLC (7n had the larger R_f; anhydrous ether) to give 17.35 mg (30% yield) of 7n and 9.02 mg (16% yield) of 8n.

Isomer Ratios for Carbamate Cycloadducts. Integration of NMR signals ($CDCl_3$) for the following purified mixtures gave the diastereomer ratios. The major isomer and signals attributable solely to it are underlined. 11a and 12a: δ 7.5-8.1 (m, 5H), 5.0-5.5 (m, 2H), 4.4-4.7 (m, 1H), 3.77 and 3.68 (2S, 3H, integration gave ratio), 3.3-3.7 (m, 2H), 1.45 (s, 9H). 11b and 12b: δ 7.5-8.1 (m, 5H), 5.0-5.6 (m, 2H), 4.4-4.7 (m, 1H), 3.79, 3.70 (2s, integration gave ratio), 3.3-3.7 (m, 2H), 1.84 (q, 2H, J = 7 Hz), 0.85 and 0.83 (2t, 3H, J = 7 Hz each). 11c and 12c: δ 7.2-8.5 (m, 9H), 6.11, 6.07 (2s, 2H), 4.5-5.7 (m, 3H), 3.68 and 3.59 (2s, integration inaccurate, approximately 2:1), 3.3-3.6 (m, 2H). 11d and 12d: δ 7.4-9.0 (m, 9H), 5.32(s, CH_2) on 5.0-6.1 (m) [4H total], 4.5-4.7 (m, 1H), 3.80 and

3.72 (2s, 3H, integration gave ratio), 3.4-3.7 (m, 2H). 7j and 8j: δ 7.4-8.0 (m, 5H), 7.37 and 7.34 (2s, 5H), 5.10 (s) on 5.0-5.7 (m) [4H total], 4.4-4.7 (m, 1H), 3.77 and 3.69 (2S, 3H, integration gave ratio), 3.3-3.6 (m, 2H).

Isomer Ratio for Cycloadducts 7m and 8m. Integration of 250 MHz NMR signals[22] ($CDCl_3$) for the purified mixture of 7m and 8m gave a 50:50 diastereomer ratio: δ 7.5-8.0 (m, 5H), 7.36 (broad s, 5H), 5.1 (m, 4H), 4.1 (m, 3H), 3.37 (m, 2H), 2.02 and 2.00 (2s, 3H, integration gave ratio) [the 2.02 signal increased on addition of acetate formed from 8l].

Preparation of 3b and 4b. A solution of phthalyl compound 7h[1d] (1.12 g, 2.7 mMol) and hydrazine hydrate (85%, 0.32 mL) was heated at 50-55°C for 7h. The resulting mixture was diluted with warm water (70 mL) and allowed to cool. Acetic acid was added (pH 5-6) and the crude product collected by filtration. Washing (cold water), digestion with 2N HCl (10 mL; 20°C), filtration, and neutralisation of the filtrate (10% $NaHCO_3$; pH 5-6) gave a white precipitate. This and a second crop obtained by concentration amounted to 0.38 g (50% yield) of pure (TLC, NMR) 3b: mp 184-85°C; IR (KBR) 2800-3550 (OH, NH_3^+), 1330 and 1115 cm^{-1} (SO_2); Found: C, 46.47; H, 4.25; N, 9.85 ($C_{11}H_{12}N_2O_5S$ requires: C, 46.65; H, 4.34; N, 9.87).

Compound 4b was prepared similar to 3b. The reaction mixture was treated with acetic acid (pH 5-6) and filtered. Unlike 3b, 4b remained in aqueous solution. Solid byproducts were removed by filtration and 2-butanol (200 mL) was added to the filtrate. After overnight cooling (0-5°C) the solid was collected and passed as an aqueous solution (25 mL of water) onto a Dowex-50W ion exchange column (H^+ form; 25 g). After water washing (600 mL), the amino acid was eluted (2N ammonia); concentration gave 0.40 g (57% yield) of pure (TLC, NMR) 4b: IR 2500-3700 (OH, NH_3^+), 1610 (br, C=O), 1330, and 1165 cm^{-1} (SO_2).

Conversion of 7a,c and 8a,c to a Mixture of 3b and 4b. A crude reaction mixture containing 7a and 8a was column chromatographed on silica gel (7a and 8a eluted together; CH_2Cl_2-acetic acid, 97:3). A portion (94 mg; 0.24 mMol) of the purified cycloadduct mixture was dissolved in a minimal amount of glacial acetic acid and treated with acetic acid-hydrogen chloride (8 mL, containing 0.08 g of HCl)[23]. After 30 min, water (10 mL) was added and all the volatiles were stripped. Water (5 mL) was added to the residue and then a few drops of 10% $NaHCO_3$ (pH 5-6). The resulting solution was washed (CH_2Cl_2) and concentrated to give 53 mg (78% yield) of a 30:70 (NMR) mixture of 3b and 4b.

A mixture of 7c and 8c (160 mg; 0.31 mMol; purified similar to 7a and 8a) was treated with a solution of trifluoroacetic acid (0.35 g) in glacial acetic acid (5 mL)[20]. Water was added and the CH_2Cl_2 layer discarded. Aqueous 10% $NaHCO_3$ was added (pH 5-6) and the water layer concentrated to give 75 mg (85% yield) of a 40:60 mixture of 3b and 4b. The ratio determined here (ring methine, near residual DOH) is considered less accurate than for the methyl esters 11c and 12c, but the major isomer is clear.

(S)-2-[(Benzyloxy)carbonyl]amino-3-buten-1-ol (6l). Vinylglycine (5a) (2g; 19.8 mMol) was added portionwise (vigorous reaction!) over 30 min to a cold (0-5°C) mixture of LAH (1.5 g; 40 mMol) and THF (40 mL) under nitrogen. The mixture was stirred 30 min at room temperature and 2h at 35°C. After cooling, wet ether and moist Na_2SO_4 were added to destroy excess LAH and hydrolyze the alcohol complex. The mixture was filtered, the filtrate was concentrated, and the crude product was Kugelrohr distilled (bp 80-100°C [10 mm]) to give 0.35 g (20% yield) of relatively pure 2-amino-3-buten-1-ol. TLC (BuOH-water-HOAc, 60:25:15) showed one main spot and a more polar minor spot. A portion (60 mg; 0.7 mMol) of this material was dissolved under nitrogen in THF (0.8 mL) containing triethylamine (72 mg). To the cooled (0-5°C) solution was added dropwise a solution of benzylchloroformate (0.12 g; 0.7 mMol) in THF (0.8mL). The resulting mixture was stirred 40 min at 0-5°C, filtered and concentrated. Preparative TLC (CH_2Cl_2-methanol, 95:5) gave 0.12 g (78% yield) of pure 6l: $[\alpha]_D^{25}$-20.47° (c 1.9, chloroform); IR (film) 3400, 3320 (br OH, NH), and 1760 cm^{-1} (br, 2 C=O); NMR ($CDCl_3$) δ 7.33 (s, 5H), 5.81 (ddd, 1H, J = 17.6, 9.7, 5.2 Hz), 5.10 (s) on 5.1-5.4 (m) [total 5H], 4.1-4.5 (m, 1H), 3.5-3.8 (m, 2H), and 2.66 (broad s, 1H).

(S)-2-[(Benzyloxy)carbonyl]amino-3-buten-1-yl Acetate (6m). A solution of 6l (0.05 g; 0.23 mMol), pyridine (2 mL), and acetic anhydride (1 mL) was stirred at 0-5°C for 4h and the volatiles were stripped. Preparative TLC (anhydrous ether) of the residue gave 53.3 mg (88% yield) of pure 6m: IR (film) 3320 (br, NH) and 1750 cm^{-1} (br, 2 C=O); NMR ($CDCl_3$) δ 7.35 (m, 5H), 5.6-6.0 (m, 1H), 5.11 (s) on 5.0-5.4 (m) [total 5H], 4.3-4.7 (m, 1H), 4.13 (d, 2H, J = 4.9 Hz), and 2.17 (s, 3H).

(S)-3-[(Benzyloxy)carbonyl]amino-2-methyl-4-penten-2-ol (6n). Methyllithium (0.8 mL of a 1.2M solution in ether; 1 mMol) was added dropwise to a cold (-70°C) solution of 6j (0.1 g; 0.40 mMol) in THF (1 mL). The solution was stirred for 2h at -70°C and then wet THF, water and 5% HCl were added sequentially. The mixture was warmed to room temperature and extracted several times. The combined extracts were washed, dried, and concentrated. Preparative TLC (CH_2Cl_2-HOAc, 95:5) gave several products including 34 mg (34% yield) of pure 6n: NMR ($CDCl_3$) δ 7.34 (s, 5H), 5.91 (ddd, 1H, J = 16.6, 8.2, 6.5 Hz), 5.11 (s) on 5.1-5.5 (m) [total 5H], 4.08 (m, 1H), 2.02 (broad s, 1H), and 1.25 and 1.21 (2s, 6H).

Conversion of 8n to 15. Methyllithium (0.14 mL of a 1.5M solution in ether; 0.2 mMol) was added dropwise to a cold (-70°C) solution of 8n (9 mg; 0.02 mMol) in THF (0.5 mL) and the solution stirred for 15 min at -70°C. After 15 min wet THF and water were added sequentially and the mixture warmed to above 0°C. Extraction, washing, drying, concentration and preparative TLC (anhydrous ether) gave 3.6 mg (57% yield) of pure 15: NMR ($CDCl_3$) δ 7.35 (s, 5H), 5.44 (m, 1H), 5.13 (m, 2H), 4.9-5.1 (m, 1H), 3.63 (d, 1H, J = 9.2Hz), 2.9-3.2 (m, 2H), 1.40 (s, 3H) and 1.22 (s, 3H).

Compound 7n was similarly transformed in 39% yield to 16: NMR ($CDCl_3$) δ 7.35 (s, 5H), 5.12 (s, 2H), 4.5-5.1 (m, 2H), 3.69 (dd, 1H, J = 9.9, 10.9 Hz), 2.95 (d, 2H, J = 9.0 Hz), and 1.32 and 1.25 (2s, 6H).

Conversion of 4b to 8j. Excess etheral diazomethane was added to a cold (0-5°C) solution of 4b (0.25 g; 0.88 mMol) in CH_2Cl_2 (30 mL) and the mixture stirred for 45 min. Concentration and preparative TLC (anhydrous ether) gave 93 mg (36% yield) of pure ester. This was dissolved in THF (1 mL) and triethylamine (41 mg) was added. The solution was cooled (0-5°C) and a solution of benzylchloroformate (64 mg; 0.38 mMol) in THF (1 mL) was added dropwise. The mixture was stirred 40 min at 0-5°C and concentrated. Preparative TLC (anhydrous ether) gave 46 mg (34% yield) of pure (NMR, TLC) 8j.

Conversion of 8j to 15. Carried out similar to the conversion of 8n to 15. Preparative TLC (anhydrous ether) gave three main products including starting material (8.3 mg; 14% recovery), an unidentified fraction, and 15 (8.1 mg; 13% yield). Compound 16 could not be detected (TLC, NMR) in either the crude mixture or separated fractions.

Epimerization of 8k. A cold (0-5°C) solution of 8h (90 mg) in CH_2Cl_2 (5 mL) was treated with excess etheral diazomethane. After 15 min the volatiles were stripped. The crude product (pure 8k; TLC and NMR) was dissolved in CH_2Cl_2 containing triethylamine (0.13 g) and the solution refluxed. NMR indicated only 8k and 17 (30:70 ratio) at 1h. No change in the ratio was observed after an additional 2h refluxing.

Preparation of Acivicin (3a) and Epimer 4a. To a warm (60-65°C) solution of 6h (0.28 g; 12.1 mMol) and dichloroformaldoxime (1.14 g; 0.1 Mol) in THF (6 mL), silver nitrate (1.28 g; 75 mMol) was added in small portions over 20 min. THF (6 mL) was also added in portions during this time as the mixture thickened. The mixture was stirred for 20 min and cooled. The silver salts were filtered off and extracted with CH_2Cl_2. The combined filtrate and extracts were washed (three 20-mL portions of 1M Na_2CO_3, then water), dried and concentrated. The residue contained mainly 13, 14 and unreacted 6h (TLC). Medium pressure (50 p.s.i.) chromatography on silica gel (Merck 60, 230-400 mesh, benzene-acetic acid, 87:13) gave 6h (51 mg; 18% recovery), 14 (127 mg), a small mixed cycloadduct fraction (11 mg; 40:60 ratio), and pure 13 (57 mg) (52% yield of cycloadducts). The purified 13 was transformed by a published procedure[24] to acivicin, identical with an authentic sample[14] (TLC, NMR and rotation).

Elemental Analyses. Due to limited quantities of material, most of the new compounds desribed here were not sent for analysis.

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