Chemistry of Oxaziridines. 5.[1] Kinetic Resolution of Sulfoxides Using Chiral 2-Sulfonyloxaziridines

Franklin A. Davis* and Joanne M. Billmers

Department of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104

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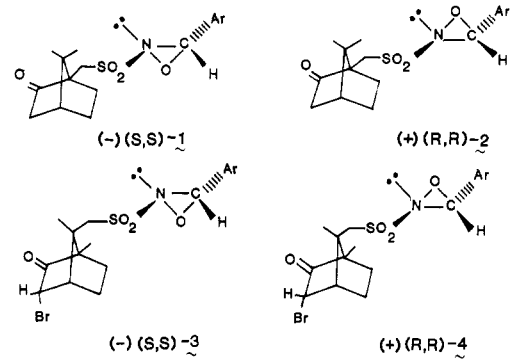
The oxidative kinetic resolution of sulfoxides **6a,b** using chiral 2-sulfonyloxaziridines **1-4** is described. When (-)-**3** and (+)-**4** are used, the configuration of the sulfoxide is controlled by the configuration of the oxaziridine three-membered ring and can be predicted by using steric arguments. With oxaziridine (-)-**1**, polar effects, in nonpolar solvents, control the sulfoxide configuration. These effects were interpreted in terms of a dipole–dipole interaction of the camphor carbonyl group in (-)-**1** and the sulfinyl sulfoxide group. Multistep oxidative kinetic resolution can be used to obtain optically active sulfoxides in up to 28% ee.

Kinetic resolution of racemic sulfoxides involves destruction of the two enantiomeric sulfoxides at different rates. Provided that the reaction does not go to completion, the less reactive enantiomer will predominate, resulting in net optical activity. Usually sulfoxide kinetic resolution involves the asymmetric oxidation of sulfoxides to sulfones,[2-4] but recently a procedure involving asymmetric reduction of sulfoxides to sulfides has been described.[5]

The asymmetric oxidation of sulfides to sulfoxides by chiral peracids and enzymatic systems frequently results in overoxidation to the sulfone.[2-4] Optical activity in the sulfoxide might, therefore, be explained by a stereoselective oxidation of the sulfide to the sulfoxide followed by preferential loss of one of the sulfoxide enantiomers by oxidation to the sulfone. Thus, an understanding of sulfoxide kinetic resolution is essential in ascertaining the degree of asymmetric induction in such chiral oxidations.

A knowledge of sulfoxide kinetic resolution is also important in understanding the mechanisms of asymmetric oxygen-transfer reactions. The chiral recognition mechanisms for the asymmetric oxidation of achiral sulfides to sulfoxides and the oxidative kinetic resolutions of sulfoxides should be related since the mechanisms for sulfide to sulfoxide and sulfoxide to sulfone oxidation are similar.[6] Indeed, Montanari and co-workers proposed similar chiral recognition mechanisms for the asymmetric oxidation of sulfides to sulfoxides and the kinetic resolution of sulfoxides using chiral peracids.[3,9] These mechanisms were based on a consideration of nonbonded steric interactions in the transition states. Polar effects were not considered or explored.

Recently, we described the synthesis of a new class of optically active oxidizing agents, chiral 2-sulfonyloxaziridine diastereomers (-)-(*S,S*)-**1** and -**3** and (+)-(*R,R*)-**2** and -**4**, where *S,S* and *R,R* refer to the configurations of the oxaziridine three-membered ring.[10] These reagents afforded much better enantioselectivity than chiral peracids or hydroperoxides for the asymmetric oxidation of sulfides to sulfoxides[10] and the asymmetric epoxidation of alkenes.[1] The configuration of the oxaziridine three-membered ring was shown to control the configuration of the products, which could be predicted by using steric arguments. The success of diastereomers **1-4** was attributed to the fact that the active-site oxygen was incorporated into a rigid three-membered ring one bond removed from the C and N chiral centers.



Oxidation of sulfides to sulfoxides using 2-sulfonyloxaziridines occurs very rapidly ($t_{1/2}$ = 0.1-1.0 min) whereas oxidation of sulfoxides to sulfones occurs slowly ($t_{1/2}$ = 10-20 h).[11] Consequently, sulfoxide kinetic resolution is not a problem in using **1-4** for asymmetric oxidations. As part of our continuing studies of the mechanisms of asymmetric oxygen transfer,[1] we report a study of oxidative sulfoxide kinetic resolution using diastereomeric 2-sulfonyloxaziridines. These studies demonstrate that polar factors play a significant role in sulfoxide kinetic resolution that has not previously been recognized. Such electronic effects have an influence on both product configuration and asymmetric induction.

Results

The oxidative kinetic resolution of methyl *p*-tolyl sulfoxide (**6a**) and *tert*-butyl phenyl sulfoxide (**6b**) was accomplished by addition of 0.5 equiv of the appropriate oxaziridine diastereomer, **1**, **3**, or **4**, to the sulfoxide. After 24 h of stirring at 25 °C, the chiral oxaziridine was com-

(1) Davis, F. A.; Harakal, M. A.; Awad, S. B. *J. Am. Chem. Soc.* **1983**, *105*, 3123.
(2) Auret, B. J.; Boyd, D. R.; Henbest, H. B. *J. Chem. Soc.* **1968**, 2374.
(3) Folli, U.; Iarossi, D.; Montanari, F. *J. Chem. Soc. C* **1968**, *1372*.
(4) Sugimoto, T.; Kokubo, T.; Miyazaki, J.; Tanimoto, S.; Okano, M. *Bioorg. Chem.* **1981**, *10*, 311.
(5) Annunziata, R.; Borgogno, G.; Montanari, F.; Quici, S.; Cucinella, S. *J. Chem. Soc., Perkin Trans. 1* **1981**, 113.
(6) Electrophilic attack of the terminal oxygen in peracids on the sulfur atom in sulfides[7] and sulfoxides[8] is the generally accepted mechanism for sulfide to sulfoxide and sulfoxide to sulfone oxidation.
(7) For a review, see: Barnard, D.; Bateman, L.; Cunneen, J. I. In "Organic Sulfur Compounds"; Kharashch, N., Ed.; Pergamon Press: Elmsford, NY, 1961; Chapter 21.
(8) Overberger, C. G.; Cummins, R. W. *J. Am. Chem. Soc.* **1953**, *75*, 4260. For an alternative, nucleophilic mechanisms, see: Oae, S.; Takata, T. *Tetrahedron Lett.* **1980**, 3213 and references cited therein.
(9) Folli, U.; Iarossi, D.; Montanari, F.; Torre, G. *J. Chem. Soc.* **1968**, 1317.
(10) Davis, F. A.; Jenkins, R. H., Jr.; Awad, S. B.; Stringer, O. D.; Watson, W. H.; Galloy, J. *J. Am. Chem. Soc.* **1982**, *104*, 5412.
(11) Unpublished results of Joanne Billmers from our laboratory.

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Table I. Oxidative Kinetic Resolution of Sulfoxides 6a,b Using Chiral 2-Sulfonyl Oxaziridines at 25 °C

entry	oxaziridine diastereomer	solvent	sulfoxide	sulfoxide product % ee	sulfoxide product config	yield, %
1	(−)-(*S,S*)-1	benzene	6a	8.6	*R*	44
2		chloroform		5.4	*R*	57
3		*o*-dichlorobenzene		0.1	*R*	84
4		pyridine		0.2	*R*	18
5		1-butanol		0.4	*S*	46
6		acetone		1.4	*S*	90
7		ethanol		3.8	*S*	52
8		acetonitrile		7.6	*S*	60
9		benzene	6b	1.2	*R*	92
10		chloroform		0.6	*R*	71
11		*o*-dichlorobenzene		1.2	*R*	80
12		pyridine		3.0	*R*	30
13		acetone		0.6	*S*	54
14		ethanol		0.9	*R*	76
15		acetonitrile		1.2	*S*	60
16	(−)-(*S,S*)-3	chloroform	6a	19.4	*S*	73
17		acetonitrile		22.0	*S*	70
18		chloroform	6b	8.0	*R*	80
19	(+)-(*R,R*)-4	benzene	6a	13.4	*R*	96
20		chloroform		17.1	*R*	60
21	(+)-(*R,R*)-4	*o*-dichlorobenzene	6a	22.0	*R*	55
22		acetone		22.0	*R*	50
23		acetonitrile		27.0	*R*	70
24		chloroform	6b	19.0	*R*	80
25		acetone		23.0	*R*	70

pletely consumed. The remaining sulfoxide was then separated from the corresponding sulfone, 7, and chiral

$$\underset{5}{ArSR} \rightarrow \underset{6}{ArS(O)R} \rightarrow \underset{7}{ArS(O)_2R}$$

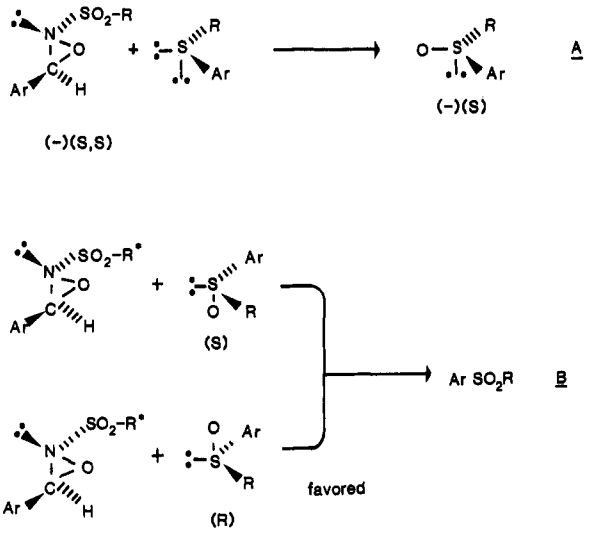
a, R = Me; Ar = *p*-tolyl
b, R = CMe_3; Ar = Ph

sulfonimine ($R^*SO_2N{=}CHAr$) by preparative TLC on silica gel. Isolated yields were good to excellent, depending on the solvent. Optical yields were determined by the chiral shift reagent method and by comparison of optical rotations with literature values. Agreement between the two methods was excellent. These results are summarized in Table I.

The optical purity of methyl *p*-tolyl sulfoxide (**6a**) obtained by kinetic resolution using (−)-**1** was in the range 0.2–8.6 % ee and for *tert*-butyl phenyl sulfoxide (**6b**), 0.6–3.0 % ee. By contrast, the enantioselectivity for the asymmetric oxidation of methyl *p*-tolyl sulfide (**5a**) and *tert*-butyl phenyl sulfide (**5b**) using (−)-**1** was considerably better: 17 and 11 % ee, respectively.[10] The lower asymmetric induction observed in the kinetic resolution of **6b** compared to that of **6a** is in accord with the group size difference (GSD) principles discussed previously for the sulfides.[10]

The dependence of sulfoxide configuration and asymmetric bias on solvent has been reported for chiral peracid oxidations of achiral sulfides. These effects are not understood,[9] and the influence of solvent on sulfoxide kinetic resolution using chiral peracids has not been described. Solvent effects were not observed for asymmetric oxidations of achiral sulfides using oxaziridine diastereomers **1**–**4**.[1,10] In contrast to these results is the effect of solvent on the kinetic resolution of sulfoxides **6a,b** by oxaziridine diastereomer (−)-(*S,S*)-**1**. Both the enantioselectivity and the configuration of these sulfoxides were solvent dependent (Table I).[12] As the polarity of the solvent increases, the configuration of sulfoxide **6a** changes from *R* to *S*. Sulfoxide **6b** appears to be subject to the same influences, but the magnitude of asymmetric induction is much less. As we have pointed out elsewhere, care should be exercised in the interpretation of results where the asymmetric bias is so low.[10]

Scheme I



When diastereomeric oxaziridines (−)-**3** and (+)-**4** are used in the oxidative kinetic resolution of **6a,b**, solvent effects were not observed. Furthermore, the enantioselectivity is of the same order of magnitude as that for asymmetric oxidations of sulfides, **5a,b**, by these reagents.[10]

Discussion

The chiral recognition mechanism proposed for the asymmetric oxidation of sulfides to sulfoxides by oxaziridine diastereomers **1**–**4** was based on a consideration of nonbonded interactions in the transition state (Scheme IA).[10] The substrate sulfur atom attacks the oxaziridine oxygen in such a way that the large (R_L) and small (R_S) groups of the sulfide (R_LSR_S) face the small and large regions of the oxaziridine three-membered ring. The 2-chloro-5-nitrophenyl group is considered to be small and

(12) For leading references to the influence of solvent effects on reaction mechanisms, see: Reichardt, C. *Angew. Chem., Intl. Ed. Engl.* **1965**, *4*, 29. Bentley, T. W.; Schleyer, P. v. R. *Adv. Phys. Org. Chem.* **1977**, *14*, 1.

the camphorsulfonyl group large. Thus, (-)-(*S,S*)-**1** and -**3** gave only sulfoxides having the *S* configurations while (+)-(*R,R*)-**2** and -**4** gave sulfoxides having the *R* configuration. Significantly, this chiral recognition was independent of both solvent and sulfide structure.

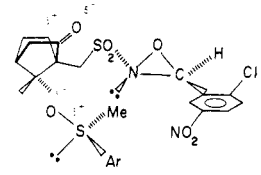
If a similar mechanism is considered for the oxidative kinetic resolution of sulfoxides **6a,b** by **1–4**, then (-)-(*S,S*)-**1** and -**3** should preferentially oxidize the (+)-*R* enantiomers of **6a,b**, resulting in enrichment of the (-)-*S* sulfoxides. Conversely, (+)-(*R,R*)-**2** and -**4** will preferentially oxidize the (-)-*S* enantiomers of **6a,b**, affording the (+)-*R* sulfoxides (Scheme IB). This assumes that the chiral recognition is controlled by minimizing nonbonded steric interactions in the transition state for oxidation of sulfoxides to sulfones.

As is evident from the results summarized in Table I, the chiral recognition mechanism outlined in Scheme IB works only for sulfoxide to sulfone oxidations when (-)-**3** and (+)-**4**, are used. These diastereomeric oxaziridines selectively oxidized the (+)-*R* and (-)-S sulfoxides of **6a,b**, respectively. The fact that the product configuration can be predicted by this model (Scheme IB) and is independent of solvent strongly suggests that the oxidation of sulfoxides to sulfones is controlled by the same factors that govern the asymmetric oxidation of sulfides to sulfoxides by **1–4**. These factors have been shown to be predominantly steric in nature.

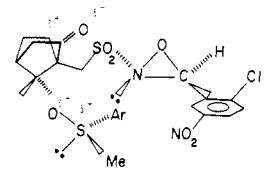
Sulfoxide oxidations using (-)-(*S,S*)-**1**, on the other hand, exhibited a strong dependence of the sulfoxide configuration and optical purity on the solvent. With this oxaziridine electronic factors are apparently more important than steric factors in determining the chiral recognition. The primary structural difference between oxaziridines (-)-**1**, (+)-**2** and (-)-**3**, (+)-**4** is the proximity of the camphor carbonyl group to the active-site oxygen. In (-)-**1** the carbonyl group is situated near the oxaziridine oxygen atom, in a position to interact with the substrate during oxidation. In (-)-**3** and (+)-**4** the carbonyl group is too far removed from the active site to have any significant influence on the course of the oxidation. The enantioselectivity of asymmetric enolate hydroxylations was previously shown to be determined by the position of the carbonyl group in **1–4**.[13] In these hydroxylations the asymmetric bias was three times greater when (-)-**1** and (+)-**2** were used than when (-)-**3** and (+)-**4** were used.

The sulfinyl group in sulfoxides is highly polar in nature and well-known to interact with other polar functionalities by dipole–dipole electrostatic and hydrogen-bonding interactions.[14] Stoichiometric complexes of dimethyl sulfoxide (Me_2SO) with water and phenols are, for example, well-known.[15] Ritchie and Pratt, using IR absorption data, have reported complexes of Me_2SO with acetone, ascribing their formation to dipole–dipole interactions.[16] The magnitude of these hydrogen-bond and dipole–dipole interactions can range from a few tenths to several kcal/mol. Since a difference of only 1.8 kcal/mol in the diastereomeric transition state for asymmetric induction at 25 °C is estimated to give 90% ee, it is not surpising that electronic effects are of importance in the oxidative kinetic resolution of sulfoxides. Although polar effects are known to influence asymmetric synthesis, they are not well understood.[17]

We beliveve that the solvent dependence (Table I) observed in the kinetic resolution of **6a** employing (-)-**1** can be explained by association of the carbonyl dipole with the sulfinyl sulfoxide dipole as shown in structures **8a,b**. This



8a [-](S) **6a**



8b [+](R) **6a**

sulfinyl–carbonyl interaction will be stronger with the (-)-(*S*)-**6a** than with (+)-(*R*)-**6a**, **8a** and **8b**, respectively, because the bulky *p*-tolyl group is in a less congested region in the former. In nonpolar solvents such as benzene and chloroform this association is strong and governs the chiral recognition. As the polarity of the solvent increases so does the interaction of the solvent with carbonyl and sulfinyl dipoles. Consequently, the interaction depicted in **8a** becomes less important and the chiral recognition is again controlled by nonbonded steric interactions. A somewhat similar interpretation was used by Harada and Matsumoto to explain the effect of solvent on the hydrogenation of chiral imines to α-amino acids.[18]

Kinetic resolution can often be used to obtain sulfoxides of high enantiomeric purity when multistep oxidation procedures are used. The first step is an asymmetric oxidation of the achiral sulfide to an optically active sulfoxide. Asymmetric oxidation of the minor sulfoxide enantiomer should then result in enrichment of the major enantiomer. The optical purity of isopropyl phenyl sulfoxide, for example, was increased from 62% to 93% by further oxidation using hydrogen peroxide in bovine serum albumin.[4]

The possibility that sulfoxides of high optical purity might be obtained in a similar manner by using chiral 2-sulfonyloxaziridines was explored. One equivalent of (+)-(*R,R*)-**4** was added to methyl *p*-tolyl sulfide (**5a**) at -50 °C in chloroform. After warming to room temperature an additional, 0.5 equiv of (+)-**4** were added. The (+)-(*R*)-**6a** was obtained with an optical purity of 25.9 % ee. The oxidative kintic resolution of **6a** by this oxaziridine gave **6a** in 17.0 % ee (Table I). Thus, the optical purity of sulfoxides can be further increased by using multistep oxidative kinetic resolution.

Conclusions. The oxidative kinetic resolution of sulfoxides, **6a,b**, by oxaziridines (-)-**3** and (+)-**4** is controlled by the same influences as observed for the asymmetric oxidation of sulfides to sulfoxides by these reagents. Thus the configuration of the sulfoxide is controlled by the configuration of the oxaziridine three-membered ring and can be predicted by using steric arguments. Polar effects are unimportant.

Polar effects in sulfoxide oxidative kinetic resolution are observed with oxaziridine (-)-**1**. In nonpolar media a dipole–dipole interaction of the carbonyl and sulfinyl sulfoxide groups determines the chiral recognition. Polar effects appear to be of significance only when both reagents have functionalities that can interact with the solvent in or near the active site in the transition state.

(13) Boschelli, D.; Smith, A. B., III; Stringer, O. D.; Jenkins, R. H., Jr.; Davis, F. A. *Tetrahedron Lett.* **1981**, *22*, 4385.
(14) Kingsbury, C. A.; Day, V. W.; Day, R. O. *J. Org. Chem.* **1980**, *45*, 5255 and references cited therein.
(15) Tommila, E.; Murto, M. L. *Acta. Chem. Scand.* **1963**, *17*, 1947. Holmes, J. R.; Kivelson, D.; Drinkard, W. C. *J. Am. Chem. Soc.* **1962**, *84*, 4677. Cairns, T.; Eglinton, G.; Gibson, D. T. *Spectrochim. Acta* **1964**, *20*, 31.
(16) Ritchie, C. D.; Bierl, B. A.; Honour, R. J. *J. Am. Chem. Soc.* **1962**, *84*, 4687. Ritchie, C. D.; Pratt, A. L. *Ibid.* **1964**, *86*, 1571.
(17) Kagan, H. B.; Fiaud, J. C. *Top. Stereochem.* **1979**, *10*, 175.
(18) Harada, K.; Matsumoto, K. *J. Org. Chem.* **1968**, *33*, 4467.

Experimental Section

Melting points were determined on a Mel-Temp apparatus and are uncorrected. ^{1}H NMR spectra were measured on Varian A-60A and JOEL FX-90Q NMR spectrometers. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. Solvents were purified by standard methods. Diastereomeric oxaziridines 1–4 were prepared as previously described[10] and were greater than 95 % ee. Sulfides were prepared by standard methods.

Oxidative Kinetic Resolution Procedure. In a 5-mL, single-necked round-bottom flask equipped with magnetic stirring bar and drying tube was placed 0.8 mmol of the appropriate sulfoxide, **6a** or **6b**, in 1 mL of the designated solvent. The chiral oxaziridine, 0.4 mmol, was added as a solid portionwise with stirring to the reaction mixture. After 24 h of stirring at 25 °C, the solvent was removed under vacuum. The residue was taken up in a minimum of $CHCl_3$ and the sulfoxide isolated by preparative TLC (silica gel) using chloroform. Methyl *p*-tolyl sulfoxide (**6a**) required a second purification by TLC, developing with pentane–chloroform (1:1).

Two-Step Kinetic Resolution Procedure. In a 10-mL, round-bottom flask equipped with a magnetic stirring bar and drying tube was placed 38 mg (0.27 mmol) of methyl *p*-tolyl sulfide (**5a**) in 1 mL of chloroform. The reaction mixture was cooled to −50 °C in a dry ice/methanol bath, and 132 mg (0.27 mmol) of oxaziridine (+)-(*R,R*)-**4** in 1 mL of chloroform was added dropwise. After 1 h of stirring at room temperature, an additional 66 mg (0.135 mmol) of oxaziridine (+)-(*R,R*)-**4** was added. The reaction mixture was allowed to stir for 24 h, and methyl *p*-tolyl sulfoxide (**6a**) was isolated as described above. The optical purity of the sulfoxide, 11.4 mg (54%), was determined to be 27.9 % ee by using a chiral shift reagent.

General Procedure for Determining Optical Purities of Sulfoxides. Optical yields were ascertained by comparing the optical rotations of sulfoxides **6a,b** obtained via kinetic resolution using chiral 2-sulfonyloxaziridines **1**, **3**, and **4** with those reported in the literature.[10] The optical yields determined in this manner were verified by comparing a series of 60- and 90-MHz ^{1}H NMR spectra ($CDCl_3$) at increasing concentration of the chiral shift reagent tris[3[(heptafluoropropyl)hydroxymethylene)]-*d*-camphorato]europium(III) derivative [Eu(hfc)$_3$]. When the shift difference of the appropriate absorption was at least 9 Hz, the peak areas were determined by integration. Agreement between the two methods was approximately ±1.0 % ee.

All asymmetric oxidations were carried out at least twice and the results averaged (Table I).

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Registry No. (−)-(*S,S*)-**1**, 81310-08-9; (+)-(*R,R*)-**2**, 81369-89-3; (−)-(*S,S*)-**3**, 81446-77-7; (+)-(*R,R*)-**4**, 81422-07-3; **6a**, 934-72-5; **6b**, 4170-71-2.

1,4-Oxazines via Intramolecular Ring Closure of β-Hydroxydiazoacetamides: Phenylalanine to Tetrahydroindeno[1,2-*b*]-1,4-oxazin-3(2*H*)-ones

D. E. McClure,* P. K. Lumma, B. H. Arison, J. H. Jones, and J. J. Baldwin

Merck Sharp & Dohme Research Laboratories, West Point, Pennsylvania 19486

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The synthesis of the tetrahydroindeno[1,2-*b*]-1,4-oxazin-3(2*H*)-one system from phenylalanine is described. Conversion of the intermediate vicinal amino alcohol to the 1,4-oxazine was accomplished via BF_3·Et_2O-catalyzed ring closure of a β-hydroxydiazoacetamide. The stereoselectivity and generality of the inter- and intramolecular Friedel–Crafts reactions of protected amino acids including homophenylalanine are presented.

Although α-diazocarbonyl compounds, which serve as precursors to α-keto carbene/carbenoid or α-diazonium carbonyl intermediates, have been used extensively in synthetic organic chemistry, there has been a recent resurgence of their utilization in intramolecular ring closure reactions.[1,2] Elegant and practical examples of this utilization include the syntheses of gibberellin/gibberellic acid[3] and thienamycin.[4] In this paper we report on the novel conversion of vicinal amino alcohols to 1,4-oxazinones through β-hydroxydiazoacetamides, specifically, the overall conversion of phenylalanine ((*R,S*), (*R*), or (*S*)) into 4,4a,5,9b-tetrahydroindeno[1,2-*b*]-1,4-oxazin-3(2*H*)-ones. In addition, further studies into the stereoselectivity and generality of the inter- and intramolecular Friedel–Crafts reactions of protected amino acids are also included.[5]

Initially, a classical conversion[6] of amino alcohols **1** through chloroacetamides **2** to the desired 1,4-oxazin-3-(2*H*)-ones was attempted (Scheme I). Although **2a** formed in good yield, treatment with various bases produced **3a** as a minor component of a complex mixture. Under the best conditions found (NaH, Me_2SO), the overall yield of **3a** from **1a** was in the range of 10–20% after chromatography. A variety of bases was examined on a probe scale, and none appeared to produce satisfactory yields of **3a** as determined by TLC analysis.[7] Use of the corresponding bromoacetamide gave similar results. Therefore, the preparation and decomposition of the related α-diazoacetamides **6** were considered as an alternative approach. Mechanistically, such an intermediate should facilitate the

(1) Smith, A. B., III; Dieter, R. K. *Tetrahedron* **1981**, *37*, 2407.
(2) Burke, S. D.; Grieco, P. A. *Org. React.* **1979**, *26*, 361.
(3) Lombardo, L.; Mander, L. N.; Turner, J. V. *J. Am. Chem. Soc.* **1980**, *102*, 6626. Hook, J. M.; Mander, L. N. Urech, R. *Ibid.* **1980**, *102*, 6628.
(4) Melillo, D. G.; Liu, T.; Ryan, K.; Sletzinger, M.; Shinkai, I. *Tetrahedron Lett.* **1981**, *22*, 913. Melillo, D. G.; Shinkai, I.; Liu, T.; Ryan, K.; Sletzinger, M. *Ibid.* **1980**, *21*, 2783. Salzmann, T. N.; Ratcliffe, R. W.; Christensen, B. G.; Bouffard, F. A. *J. Am. Chem. Soc.* **1980**, *102*, 6161.
(5) McClure, D. E.; Arison, B. H.; Jones, J. H.; Baldwin, J. J. *J. Org. Chem.* **1981**, *46*, 2431.
(6) Anderson, P. S.; Baldwin, J. J.; McClure, D. E.; Lundell, G. F.; Jones, J. H. *J. Org. Chem.* **1982**, *47*, 2184.
(7) In two instances yields of 40–50% of **3b** were obtained from **1b** by using potassium *tert*-butoxide in THF. However, this yield was not consistent, and in most instances the conversion of **1a** to **3a** proceeded in less than 10% yields.

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