mp 86–88 °C; IR ($CHCl_3$) 3610, 3450, 2925, 2850, 1760, 1460, 1390, 1220, 1030, 970 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, J = 6.7 Hz, 3 H), 1.26 (s, 22 H), 2.05 (m, 2 H), 3.85 (m, 1 H), 4.10 (t, J = 6.0 Hz, 1 H), 4.37 (m, 1 H), 5.40 (dd, J = 7.1, 15.4 Hz, 1 H), 5.62 (NH), 5.85 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.09, 22.67, 28.99, 29.20, 29.34, 29.45, 29.60, 29.66, 31.90, 32.36, 56.25, 66.37, 73.22, 126.51, 136.57, 160.23; CIMS ((M + 1)/z) 328, 327, 326, 325, 324. Anal. Calcd for $C_{19}H_{35}NO_3$: C, 70.54; H, 10.29. Found: C, 70.12; H, 10.79.

***dl-erythro*-Triacetylsphingosine (28).** To a solution of oxazolone **48** (0.007 g, 0.021 mmol) in glyme (3 mL) and water (1 mL) was added barium hydroxide octahydrate (0.017 g, 0.053 mmol). After refluxing for 30 h, the mixture was cooled to room temperature and gaseous CO_2 was bubbled through the solution to precipitate the barium salts. Filtration of the mixture and concentration of the filtrate in vacuo afforded crude *dl-erythro*-spingosine (**27**). This material was dissolved in acetic anhydride (1 mL) and pyridine (1 mL), and the solution was stirred at room temperature for 8 h. Concentration of the reaction mixture in vacuo and purification of the residue by preparative TLC ($CHCl_3$/MeOH/9/1) gave *dl-erythro*-triacetylsphingosine (**28**) which was identical (TLC, IR, ^1H NMR) with material prepared from naturally derived *erythro*-D-sphingosine.[31] A sample recrystallized from CH_2Cl_2/hexane had mp 90–92 °C (lit.[26] mp 91–92 °C).

Acknowledgment. We thank the National Science Foundation for support of this research (CHE-81-00132). We are grateful to Professors Clayton Heathcock and Clark Still for important discussions about this research. S.M.W. thanks the John Simon Guggenheim Memorial Foundation for a Fellowship (1983–84).

Supplementary Material Available: Complete X-ray data for compound **5a** (9 pages). Ordering information is given on any current masthead page.

Stereocontrolled Synthesis of Unsaturated Vicinal Diamines from Diels–Alder Adducts of Sulfur Dioxide Bis(imides)

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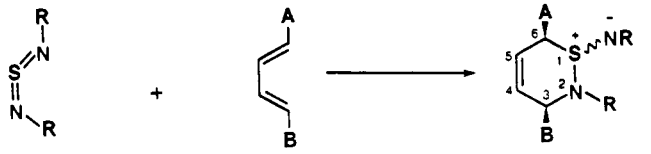
Abstract: As an extension of methodology previously developed for the synthesis of vicinal amino alcohols, stereocontrolled synthesis of unsaturated vicinal diamines from Diels–Alder adducts of sulfur dioxide bis(imides) (**1a**, **1b**) and various 1,3-dienes was investigated. The 3,6-dihydrothiazin-1-imine Diels–Alder adducts having a trans relationship of the sulfur and C-6 substituents stereospecifically afforded unsaturated vicinal diamines in high yields via ring opening with phenylmagnesium bromide to allylic sulfilimines which underwent [2,3]-sigmatropic rearrangement to sulfenamides. Desulfurization of the sulfenamide with trimethyl phosphite afforded (*E*)-threo diamines **11** and **12** from the Diels–Alder adducts of (*E*,*E*)-hexadiene **4** and **6**, respectively, and (*E*)-erythro diamines **18** and **19** from the adducts of (*E*,*Z*)-hexadiene **7** and **9**, respectively. In contrast, the epimeric thiazinimines **3** and **10**, having a cis relationship of the sulfur and C-6 substituents, were relatively unreactive toward carbon nucleophiles, affording the expected diamine derivatives in only fair to poor yields. However, the "unreactive" *cis*-thiazin-1-imines **3**, **5**, **8**, and **10** were found to undergo a facile thermal [2,3]-sigmatropic rearrangement to give thiadiazolidines **21**, **22**, **23**, and **24**, respectively, which were converted to the desired unsaturated diamine derivatives **11**, **12**, **18**, and **19** by sodium borohydride reduction in excellent yields. The reactivities of the Diels–Alder adducts are explained on the basis of the stereostructures of the Diels–Alder adducts, which were unambiguously determined by single-crystal X-ray analyses and ^1H NMR lanthanide induced shift studies. The Diels–Alder reaction of 1,3-cyclohexadiene and bis(imide) **1b** was investigated, leading to cis-vicinal carbamate **33** in a good yield along with the interesting amino diene derivative **32**.

Recent publications from these laboratories have described a diastereoselective approach to synthesis of unsaturated amino alcohol derivatives based upon Diels–Alder adducts of *N*-sulfinyl dienophiles.[1] We now report an extension of this general methodology to preparation of unsaturated vicinal diamines which allows total control of both relative and double bond configuration. The strategy outlined in this paper centers upon the propensity of readily available bis(imides) of sulfur dioxide **1a**,**b** to react with 1,3-dienes in Diels–Alder fashion[2] to produce 3,6-dihydrothiazin-1-imines (**2**) (Scheme I).[3] Although this type of cycloaddition has been known for a number of years, subsequent chemistry of adducts such as **2** has received scant attention.

Scheme I



1a R = Ts
1b R = CO_2Me

2

Since one of the primary objectives of this research program has been to develop diastereoselective routes to *acyclic* molecules, we have concentrated on developing the methodology with adducts of acyclic 1,3-dienes. Thus, bis(sulfonimide) **1a**, prepared in situ from disproportionation of *N*-sulfinyl-*p*-toluenesulfonamide as described by Kresze,[5] added to (*E*,*E*)-2,4-hexadiene at room temperature in benzene gives a chromatographically separable mixture of adducts **3** and **4** (91%) in a 1.1:1 ratio. Interestingly, Mock and Nugent[6] observed a very different ratio of **3** and **4** in

(1) (a) Garigipati, R. S.; Weinreb, S. M. *J. Am. Chem. Soc.* **1983**, *105*, 4499. (b) Garigipati, R. S.; Freyer, A. J.; Whittle, R. R.; Weinreb, S. M. *J. Am. Chem. Soc.*, preceding paper in this issue.

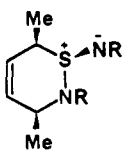
(2) For reviews of this type of cycloaddition, see: Kresze, G.; Wucherpfennig, W. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 49. Weinreb, S. M.; Staib, R. R. *Tetrahedron*, **1982**, *38*, 3087.

(3) It should be noted that a conceptually similar approach to vicinal diamines has been briefly described (Sharpless, K. B.; Singer, S. P. *J. Org. Chem.* **1976**, *41*, 2504) based upon Diels–Alder chemistry of a bis(sulfonimide) of selenium. However, these authors did not investigate the stereochemistry of the process, and yields were not impressive in the examples reported.

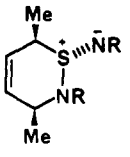
(4) For other routes to vicinal diamines, see: Gasc, M. B.; Lattes, A.; Perie, J. J. *Tetrahedron* **1983**, *39*, 703. Kohn, H.; Jung, S.-H. *J. Am. Chem. Soc.* **1983**, *105*, 4106 and references cited in these articles. See also: Fraenkel, G.; Pramanik, P. *J. Org. Chem.* **1984**, *49*, 1316. Jung, S.-H.; Kohn, H. *Tetrahedron Lett.* **1984**, *25*, 399.

(5) Wucherpfennig, W.; Kresze, G. *Tetrahedron Lett.* **1966**, 1671.

0002-7863/84/1506-7867$01.50/0



3 R=Ts
5 R=CO_2Me

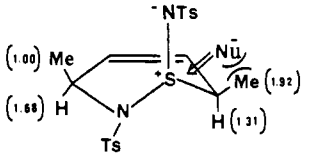


4 R=Ts
6 R=CO_2Me

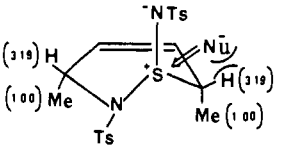
this same reaction. It is not presently clear exactly what factors (for example, bis(imide) configuration[7]) play major roles in inducing sulfur stereochemistry in these Diels–Alder adducts, nor can we rationalize the difference between our results and those of Mock and Nugent.

As discussed below, it was found that the configuration at sulfur in the 3,6-dihydrothiazin-1-imines is instrumental in controlling subsequent transformations. Thus, in order to fully understand the chemistry to be presented, it became necessary to unambiguously establish both configuration and conformation of some of the different adducts prepared. The stereochemistry of adduct **3** was therefore proven by single-crystal X-ray analysis.

The conformation of the adduct in the crystal is shown in **3′**.



3′



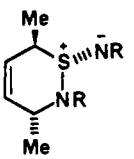
4′

As found for closely related 3,6-dihydrothiazine 1-oxides, the S–N bond of this heterocycle is quasi-axial, probably due to an anomeric effect.[1] ^1H NMR experiments with $Eu(fod)_3$ indicated that this same conformation is probably preferred in solution. Relative induced shifts for several protons are shown in parentheses and are best interpreted by assuming lanthanide complexation occurs at the imino nitrogen of **3**, although these experiments are by no means unambiguous.

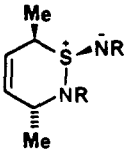
By analogy with **3′**, adduct **4** should have the conformation shown in **4′**. This assumption was supported by LIS experiments which gave the relative shifts shown in the drawing.

Cycloaddition of (*E,E*)-2,4-hexadiene with bis(carbamate) **1b**[8] at room temperature afforded a 1:8 mixture of adducts **5** and **6**, respectively. The stereochemistry of **3**–**6** was correlated by proton NMR which showed characteristic splitting patterns. In particular, the "cis" adducts **3** and **5** displayed the C-4, C-5 olefinic protons as two distinct multiplets, whereas in adducts **4** and **6** the olefinic protons appeared as a broad singlet. These assignments are in accord with the subsequent chemistry of the systems (vide infra). Although not directly proven, it seems likely from the identical reactivity of the tosyl and carbamate series that **3** and **5**, as well as **4** and **6**, have similar conformations.[9]

The Diels–Alder reactions of **1a,b** with (*E,Z*)-2,4-hexadiene proved as puzzling as the above results with respect to ratios of sulfur epimers. Thus, the (*E,Z*)-diene reacted with bis(sulfonimide) **1a** to produce adduct **7** as the major cycloaddition product (~70%) along with a few percent of the minor isomer **8**, which could not be fully purified. An X-ray crystal structure determination firmly established that the major adduct does have the stereochemistry shown in **7**. The crystal structure indicates that the dihydrothiazine ring of **7** has virtually the same conformation

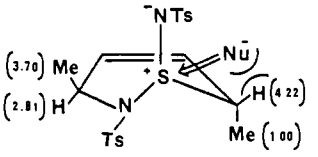


7 R=Ts
9 R=CO_2Me

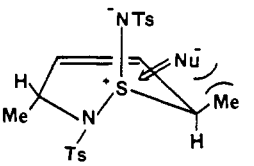


8 R= Ts
10 R=CO_2Me

as that of **3** (cf. **7′**). In addition, the S–N bond in **7** is again



7′

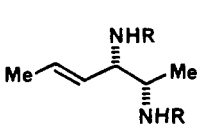


8′

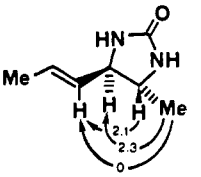
quasi-axial because of an anomeric effect. LIS experiments are generally in line with conformation **7′** in solution, and some relative europium-induced shifts are shown in the drawing. We believe that the epimeric adduct **8** probably exists in the conformation **8′**, but since this compound could not be fully purified it was not possible to prove this assumption.

Addition of bis(carbamate) **1b** to (*E,Z*)-2,4-hexadiene gave a 2.4:1 mixture of adducts **10** and **9**, respectively, in 65% yield. The carbamate and tosyl series of adducts could be correlated stereochemistry as in the previous cases by the splitting patterns of the olefinic protons in the ^1H NMR spectra.

With a variety of well-characterized Diels–Alder adducts in hand, we proceeded to investigate transformations of these systems to the desired unsaturated vicinal diamine derivatives. Treatment of adduct **4** with phenylmagnesium bromide in THF at −60 °C gave a product which without purification was refluxed in methanol-containing trimethyl phosphite to give a *single* vicinal sulfonamide **11** (83%). That the double bond of this compound



11 R=Ts
12 R=CO_2Me



13

had the *E* configuration was evident from the olefinic proton coupling constant (J = 15 Hz). The threo configuration was assigned to **11** based upon mechanistic reasoning and by analogy with vicinal carbamate **12** (vide infra).

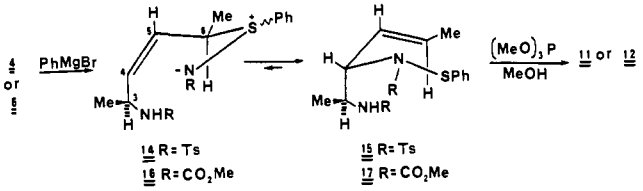
To our surprise, when epimeric adduct **3** was treated with excess phenylmagnesium bromide at temperatures up to 0 °C, no reaction occurred. However, if this adduct was instead treated with phenyllithium in THF (3 equiv, −60 °C), followed by methanolic trimethyl phosphite, a 51% yield of **11** was isolated. If methyllithium (2.5 equiv) was used, **11** was produced in 71% yield.

Similar chemistry was observed for the carbamate-substituted adduct **6**. Thus, this compound reacted cleanly with phenylmagnesium bromide (−60 °C), followed by trimethyl phosphite/methanol, to afford (*E*)-threo-vicinal carbamate **12** (92%). The stereochemistry of **12** was proven to be threo by proton nuclear Overhauser effect difference spectroscopy on the derived cyclic urea **13**.[10] Some of the significant percent enhancements are indicated in the drawing. Since epimeric Diels–Alder adduct **5** was produced in only small quantities, the above reaction sequence was not investigated in this case.

The transformations of the dihydrothiazine imines **3**, **4**, and **6** to **11** and **12** involve an initial ring opening by the organometallic

(6) Mock, W. L.; Nugent, R. M. *J. Am. Chem. Soc.* **1975**, *97*, 6521.
(7) Munsterer, H.; Kresze, G.; Lamm, V.; Gieren, A. *J. Org. Chem.* **1983**, *48*, 2833. Acyclic sulfur bis(imides) generally have the *E,Z* configuration shown in **1**.
(8) Levchenko, E. S.; Balon, Y. G.; Kirsanov, A. V. *J. Org. Chem. USSR* (*Engl. Transl.*) **1967**, *3*, 2014. See also: Kresze, G.; Munsterer, H. *J. Org. Chem.* **1983**, *48*, 3561.
(9) The dihydrothiazine rings in **4** and **6** may be more "boat-like" by analogy with the related dihydrothiazine-1-oxide,[1] but such a conformation would not be incompatible with the reactivity arguments presented here.
(10) We are grateful to A. Freyer for performing these experiments.

Scheme II

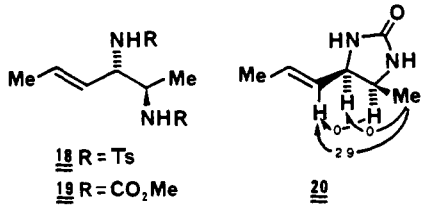


reagent to form an allylic sulfilimine (Scheme II).[11] Assuming that nucleophilic ring cleavage of these adducts occurs via the conformations discussed above and through a S_N2-like process at sulfur,[12] one can rationalize the lack of reactivity of sulfur epimer **3** vs. that of **4** toward phenylmagnesium bromide on steric grounds. Thus, a nucleophile adding to the ring sulfur of **3′** (see $Nu^- \Rightarrow$ in drawing) experiences a torsional interaction with a methyl group, whereas in **4′** only a nucleophile–hydrogen torsional interaction results. However, more reactive and/or smaller reagents such as phenyl or methyllithium are capable of opening the dihydrothiazine ring of **3**. Interestingly, in related chemistry of dihydrothiazine 1-oxides reported in the accompanying paper,[1b] no difference was observed in the rate of ring opening of sulfur epimers. Dihydrothiazine oxides generally appear to be somewhat more reactive toward nucleophiles than do the corresponding dihydrothiazinimines, probably for reasons of electronegativity.

The allylic sulfilimine **14** which is formed undergoes a [2,3]-sigmatropic rearrangement to produce sulfenamide **15**, which is cleaved by phosphite to bis(sulfonamide) **11**. Although [2,3]-sigmatropic rearrangements of allylic sulfilimines are known,[13,14] the reaction has received much less attention than the corresponding allylic sulfoxide rearrangement.[15] Assuming that the sulfilimine rearrangement proceeds via an envelope-like transition state as does the sulfoxide process[15] and that the methyl substituent at C-6 is quasi-equatorial,[1b] one can rationalize formation of **15** and subsequently the (*E*)-threo-vicinal sulfonamide **11**.

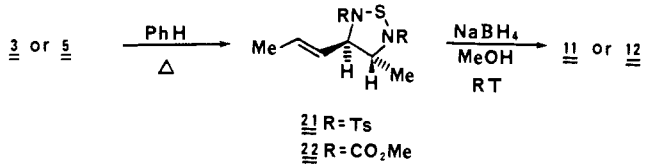
This sequence was investigated in more detail with the carbamate adduct **6**. Treatment of **6** with phenylmagnesium bromide gave a stable, isolable product characterized as sulfenamide **17**. The intermediate allylic sulfilimine **16** was not detected. Whereas the equilibrium in the allylic sulfoxide/sulfenate ester system lies to the side of the sulfoxide,[15] the reverse is true in the allylic sulfilimine/sulfenamide case, and one only detects the sulfenamide.[16] This fact is significant in some of the rearrangement chemistry outlined below.

When adduct **7**, formed from **1a** and (*E*,*Z*)-hexadiene, was treated with phenylmagnesium bromide followed by methanolic trimethyl phosphite, the (*E*)-erythro-vicinal sulfonamide **18** was

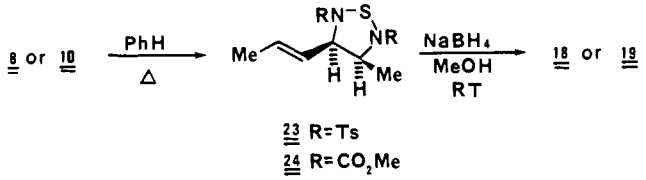


cleanly formed in 71% yield. Similarly, carbamate adduct **9** gave exclusively (*E*)-erythro-vicinal carbamate **19** (94%). The erythro

Scheme III



Scheme IV



stereochemistry was proven by cyclization of **19** to urea **20** which was investigated by ^1H NOEDS methods.[10] The observed percent enhancements shown in the drawing are fully in accord with the assigned stereochemistry.

Epimeric Diels–Alder adduct **10** did not react with phenylmagnesium bromide. Treatment of **10** with either phenyllithium or methyllithium at −60 °C, followed by trimethyl phosphite in methanol, did give **19**, but in only 38% yield.

The results in the (*E*,*Z*)-hexadiene-derived adduct series can be explained by using the type of rationale presented above. Inspection of conformations **7′** and **8′** reveals that an entering nucleophile ($Nu^- \Rightarrow$) will experience the same sort of torsional interactions as in **4′** and **3′**, respectively. Therefore, it seems reasonable to expect that **10** would react sluggishly with various organometallics, and that **7** and **9** would react more readily to form the allylic sulfilimines. [2,3]-Sigmatropic rearrangement of these sulfilimines proceeds as shown in Scheme II, except that the intermediates are now epimeric at C-3, producing the *E*-erythro series of products.

In view of the fact that various Diels–Alder adducts **2** having a cis relationship of the sulfur and C-6 substituents were relatively unreactive toward carbon nucleophiles, producing diamine derivatives in only fair to poor yields, we were prompted to investigate some alternative methodology. It was discovered that refluxing "unreactive" adduct **3** in benzene for 2.5 h produced stable thiadiazolidine **21** in quantitative yield. The structure of **21** was proven by its sodium borohydride reduction to (*E*)-threo-vicinal sulfonamide **11** (94%) (Scheme III). Similarly, "unreactive" carbamate adduct **5** on heating in benzene for 1 h afforded thiadiazolidine **22** (96%). Sodium borohydride reduction of **22** yielded (*E*)-threo-vicinal carbamate **12** (91%).

This transformation involves a novel type of [2,3]-sigmatropic rearrangement which has not previously been observed. Since 3,6-dihydrothiazinimines exist in conformations having a quasi-axial *S*–N bond (vide supra), these compounds are properly disposed stereoelectronically for such an electrocyclic process. As mentioned above, the equilibrium in the allylic sulfilimine rearrangement lies to the side of the sulfenamide, which corresponds to the thiadiazolidines **21** and **22**. That this is a remarkably facile rearrangement is evidenced by the detection of about 11% of thiadiazolidine **22** as a side product in the room temperature Diels–Alder reaction of (*E*,*E*)-2,4-hexadiene and **1b** used to produce adducts **5** and **6**.

Application of this rearrangement to "unreactive" adducts **8** and **10** in the (*E*,*Z*)-hexadiene series afforded thiadiazolidines **23** and **24**, respectively, in high yield under identical conditions. Sodium borohydride reduction of these compounds cleanly afforded the (*E*)-erythro-vicinal diamine derivatives **18** and **19** (Scheme IV). It should also be noted that upon reexamination of the Diels–Alder cycloaddition used to prepare carbamate-substituted adducts **9** and **10**, 7% of thiadiazolidine **24** could be isolated. Thus, all those Diels–Alder adducts which did not react cleanly with organometallic reagents could efficiently be transformed to the desired products via this [2,3]-sigmatropic rearrangement.

(11) For a review of sulfilimine chemistry, see: Gilchrist, T. L.; Moody, C. J. J. *Chem. Rev.* **1977**, *77*, 409.

(12) Cram, D. J.; Day, J.; Rayner, D. R.; von Schriltz, D. M.; Duchamp, D. J.; Garwood, D. C. *J. Am. Chem. Soc.* **1970**, *92*, 7369 and references cited therein.

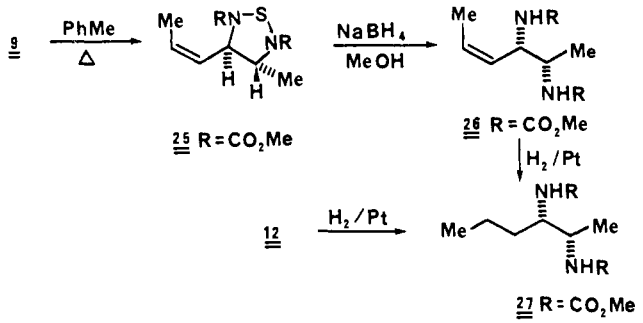
(13) Ash, A. S. F.; Challenger, F.; Greenwood, D. *J. Chem. Soc.* **1951**, 1877. Ash, A. S. F.; Challenger, F. *Ibid.* **1952**, 2792. Briscoe, P. A.; Challenger, F.; Duckworth, P. S. *Ibid.* **1956**, 1755.

(14) Kakimoto, M.; Yamamoto, T.; Okawara, M. *Tetrahedron Lett.* **1979**, 623. Cvetovich, R. J. Ph.D. Thesis, Columbia University, **1979**. Petranek, J.; Vecera, M. *Collect. Czech. Chem. Commun.* **1959**, *24*, 2191.

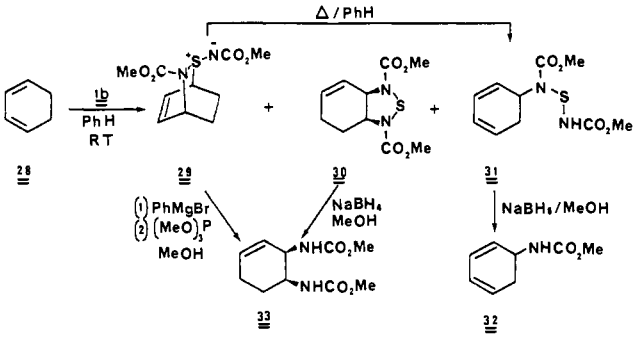
(15) Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147. Hoffman, R. W. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 563.

(16) In particular see footnote 5 in: Sharpless, K. B.; Hori, T. *J. Org. Chem.* **1976**, *41*, 176.

Scheme V



Scheme VI



In an attempt to further extend the scope of this synthetic methodology, the *reactive* Diels–Alder adduct **9** was heated in toluene (7 h). As anticipated, the product of this reaction was thiadiazolidine **25** having the *Z*-threo configuration. Unfortunately, the yield here was only 28%. The *Z* double bond configuration was established by the vinyl coupling constant (J = 10 Hz). Reduction of **25** with sodium borohydride gave (*Z*)-threo-vicinal carbamate **26** (95%). The stereochemistry of **26** was proven by catalytic hydrogenation to threo-compound **27** which was identical with a sample prepared by double bond hydrogenation of *E*-threo isomer **12** (Scheme V).

On thermolysis, adduct **6** which is derived from (*E*,*E*)-hexadiene would be expected to rearrange to the (*Z*)-erythro-thiadiazolidine. However, on heating **6** in toluene for several hours only extensive decomposition was observed. We do not presently understand why those Diels–Alder adducts which react readily with organometallics do not cleanly rearrange to thiadiazolidines. Since these systems should produce (*Z*)-alkenes, it is possible that unfavorable nonbonded interactions in the [2,3]-sigmatropic rearrangement transition state change the course of the reaction.

In order to gauge whether this methodology will also apply to cyclic dienes, bis(imide) **1b** was added at room temperature to 1,3-cyclohexadiene (**28**). The reaction produced a single Diels–Alder adduct (**29**, 42%), thiadiazolidine (**30**, 29%), and amino diene derivative (**31**, 8%) (Scheme VI). We believe that adduct **29** has the exo stereochemistry based upon the fact that when it was heated in benzene (2 h) *only* elimination product **31** was formed (100% yield).[17] The epimeric endo Diels–Alder adduct probably rearranges to thiadiazolidine **30** by a [2,3]-sigmatropic process as it is formed in the cycloaddition reaction. Compound **31** can be reduced cleanly with methanolic sodium borohydride to the interesting amino diene derivative **32**, which we believe may eventually prove useful in aminocyclitol synthesis. Sodium borohydride reduction of thiadiazolidine **30** gave *cis*-vicinal carbamate **33** (91%). Diels–Alder adduct **29** reacted readily with phenylmagnesium bromide, followed by methanolic phosphite, to afford **33** (85%).

Thus, using the chemistry outlined in this paper, it is possible to predictably generate a variety of stereochemically pure unsaturated vicinal diamine derivatives from 1,3-dienes of known geometry. We are currently investigating extensions and applications of this methodology.

(17) It is conceivable that **31** is formed from cyclohexadiene in an ene-reaction,[7] but more likely is produced during the cycloaddition by thermal elimination of Diels–Alder adduct **29**.

Experimental Section

Reaction of *N*,*N*′-Bis(*p*-toluenesulfonyl)sulfur Diimide (1a) with (*E*,*E*)-2,4-Hexadiene. A solution of dry pyridine (0.008 mL) in dry benzene (0.08 mL) was added at room temperature to a solution of *N*-sulfinyl-*p*-toluenesulfonamide (0.880 g, 4.1 mmol) in dry benzene (1.5 mL), and the mixture was stirred at room temperature for 1 h, during which time **1a** formed as a pale yellow crystalline precipitate.[5] The entire mixture was diluted with dry benzene (15 mL), and (*E*,*E*)-2,4-hexadiene (0.45 mL, 3.9 mmol) was added. After the mixture was stirred at room temperature for 15 h, the solvent was evaporated in vacuo. The residue was chromatographed on silica gel eluting with hexane–ethyl acetate (1:1) to give isomeric dihydrothiazinimines **3** (0.44 g, 48%) and **4** (0.39 g, 43%).

Data for 3 (less polar isomer): colorless prisms from ethyl acetate; mp 155–156 °C; IR (Nujol) 1600, 1300, 1165, 1140, 1090, 1000, 880, 780, 740, 670 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.09 (3 H, d, J = 7.1 Hz), 1.29 (3 H, d, J = 7.0 Hz), 2.39 (3 H, s), 2.47 (3 H, s), 3.64 (1 H, m), 4.48 (1 H, m), 5.47 (1 H, m), 5.80 (1 H, m), 7.1–7.9 (8 H, m); mass spectrum, m/z (relative intensity) 452 [M$^+$] (1.6), 297 (72.7), 224 (4.1), 198 (4.1), 155 (45.6), 141 (16.7), 126 (11.0), 100 (30.3), 91 (100.0), 81 (6.0), 65 (14.6). Anal. Calcd for $C_{20}H_{24}N_2O_4S$: C, 53.07; H, 5.34. Found: C, 52.99; H, 5.31.

Data for 4 (more polar isomer): colorless prisms from ethyl acetate/hexane; mp 147–148 °C; IR (Nujol) 1600, 1300, 1160, 1150, 1080, 1000, 880, 760, 740, 680, 660 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) 1.37 (3 H, d, J = 7.0 Hz), 1.50 (3 H, d, J = 7.0 Hz), 2.40 (3 H, s), 2.44 (3 H, s), 3.51 (1 H, m), 4.19 (1 H, m), 5.76 (2 H, br s), 7.2–7.8 (8 H, m); mass spectrum, m/z (relative intensity) 452 [M$^+$] (1.0), 297 (85.0), 224 (2.0), 198 (1.8), 171 (10.3), 155 (34.9), 141 (8.6), 139 (10.6), 126 (8.3), 100 (13.4), 91 (100.0), 82 (20.1). Anal. Calcd for $C_{20}H_{24}N_2O_4S$: C, 53.07; H, 5.14. Found: C, 52.97; H, 5.29.

Reaction of *N*,*N*′-Bis(methoxycarbonyl)sulfur Diimide (1b) with (*E*,*E*)-2,4-Hexadiene. To a solution bis(imide) **1b** (0.570 g, 3.2 mmol)[8] in dry benzene (6 mL) was added (*E*,*E*)-2,4-hexadiene (0.370 mL, 3.2 mmol) at room temperature with stirring. The mixture was stirred for 17 h at room temperature, and the solvent and partially evaporated to give adduct **6** as colorless crystals (0.530 g, 64%). The mother liquor was concentrated, and the residue was chromatographed on silica gel eluting with hexane–ethyl acetate (1:1) to first give thiadiazolidine **22** as a pale yellow oil (0.093 g, 11%), whose IR, ^{1}H NMR, and mass spectrum were identical with those of the compound obtained by thermolysis of Diels-Alder adduct **5**.

Further elution with hexane–ethyl acetate (1:3) followed by ethyl acetate gave minor Diels–Alder adduct **5** (0.073 g, 9%) and additional major adduct **6** (0.060 g, 7%; combined yield of **6**, 71%).

Data for 6: colorless prisms from ethyl acetate–ether; mp 120–121 °C; IR (Nujol) 1730, 1640, 1290, 1260, 1240, 1200, 1070, 940, 880, 780, 740 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.47 (3 H, d, J = 6.4 Hz), 1.51 (3 H, d, J = 7.1 Hz), 3.65 (3 H, s), 3.65 (1 H, m), 3.94 (3 H, s), 4.29 (1 H, m), 5.91 (2 H, br s); mass spectrum, m/z (relative intensity) 260 [M$^+$] (24.7), 187 (20.0), 144 (93.0), 96 (27.9), 82 (100.0), 67 (90.1), 59 (49.9). Anal. Calcd for $C_{10}H_{16}N_2O_4S$: C, 46.14; H, 6.20. Found: C, 46.34; H, 6.16.

Data for 5: colorless prisms from ethyl acetate/ether; mp 75–77 °C; IR (Nujol) 1720, 1640, 1320, 1280, 1250, 1150, 1100, 1070, 960, 860, 790, 770 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.43 (3 H, d, J = 6.9 Hz), 1.51 (3 H, d, J = 7.2 Hz), 3.68 (3 H, s), 3.81 (1 H, m), 3.93 (3 H, s), 4.52 (1 H, m), 5.5–5.6 (1 H, m), 5.92 (1 H, m); mass spectrum, m/z (relative intensity) 260 [M$^+$] (26.2), 144 (100.0), 128 (31.3), 102 (51.6), 82 (55.0), 67 (61.0), 59 (54.9). Anal. Calcd for $C_{10}H_{16}N_2O_4S$: C, 46.14; H, 6.20. Found: C, 45.94; H, 6.08.

Reaction of Bis(imide) 1a with (*E*,*Z*)-2,4-Hexadiene. Dihydrothiazines **7** and **8** were obtained by reaction of bis(imide) **1a** (0.41 g, 1.1 mmol)[5] with (*E*,*Z*)-2,4-hexadiene (0.23 mL, 2.0 mmol) by the procedure described above for the (*E*,*E*)-diene. In this case, the major isomer **7** (0.320 g, 65%) crystallized directly from the reaction mixture. The mother liquor was concentrated, and the residue was partially purified by chromatography on silica gel to give an inseparable 1:1 mixture of epimeric adducts **7** and **8** (0.062 g, 13%).

Data for 7: colorless prisms from ethyl acetate; mp 202–203 °C; IR (Nujol) 1600, 1300, 1170, 1150, 1080, 990, 880, 850, 820, 760, 740, 670 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.06 (3 H, d, J = 7.0 Hz), 1.26 (3 H, d, J = 7.1 Hz), 2.39 (3 H, s), 2.47 (3 H, s), 3.57 (1 H, m), 4.44 (1 H, m), 5.76–5.93 (2 H, m), 7.2–8.0 (8 H, m); mass spectrum, m/z (relative intensity) 452 [M$^+$] (0.4), 297 (100), 283 (4.3), 249 (3.9), 224 (5.4), 171 (14.0), 155 (68.8), 141 (27.3), 139 (16.2), 128 (15.1), 126 (22.2), 100 (17.9), 91 (83.1), 82 (34.4). Anal. Calcd for $C_{20}H_{24}N_2O_4S$:

C, 53.07; H, 5.34. Found: C, 52.99; H, 5.34.

Data for 8: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.21 (3 H, d, J = 7.0 Hz), 1.38 (3 H, d, J = 7.0 Hz), 2.39 (3 H, s), 2.44 (3 H, s), 4.1 (2 H, m), 5.4 (1 H, m), 5.7 (1 H, m), 7.2–8.0 (8 H, m).

Reaction of Bis(imide) 1b with (*E*,*Z*)-2,4-Hexadiene. Addition of **1b** (0.450 g, 2.5 mmol) to (*E*,*Z*)-2,4-hexadiene (0.790 mL, 6.9 mmol), by the procedure described for the (*E*,*E*)-diene gave the thiadiazolidine **24** as a pale yellow oil (0.046 g, 7%) whose IR and ^{1}H NMR spectra were identical with those of material obtained by thermolysis of Diels–Alder adduct **10**, the adduct **10** (0.301 g, 46%), and the isomeric adduct **9** (0.124 g, 19%).

Data for 10: colorless prisms from ethyl acetate–ether; mp 107–109 °C; IR (Nujol) 1720, 1660, 1300, 1290, 1230, 1140, 1070, 950, 870, 770 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.42 (3 H, d, J = 6.4 Hz), 1.52 (3 H, d, J = 7.3 Hz), 3.66 (3 H, s), 3.93 (3 H, s), 3.93 (1 H, m), 4.38 (1 H, m), 5.54 (1 H, m), 6.09 (1 H, m); mass spectrum, m/z (relative intensity) 260 [M$^+$] (34.3), 144 (100.0), 100 (26.2), 82 (46.1), 67 (36.9), 59 (31.7). Anal. Calcd for $C_{10}H_{16}N_2O_4S$: C, 46.14; H, 6.20. Found: C, 46.10; H, 6.10.

Data for 9: colorless prisms from ethyl acetate–ether; mp 89–91 °C; IR (Nujol) 1720, 1630, 1320, 1260, 1200, 1080, 960, 940, 870, 790, 735 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.41 (3 H, d, J = 7.2 Hz), 1.45 (3 H, d, J = 7.0 Hz), 3.65 (1 H, m), 3.68 (3 H, s), 3.94 (3 H, s), 4.52 (1 H, m), 5.92 (2 H, br s); mass spectrum, m/z (relative intensity) 260 [M$^+$] (35.0), 144 (100.0), 100 (24.2), 82 (63.8), 67 (57.2), 59 (38.5). Anal. Calcd for $C_{10}H_{16}N_2O_4S$: C, 46.14; H, 6.20. Found: C, 45.75; H, 6.08.

(±)-(*R,*R**-(*E*)]-4,5-Bis[[(4-methylphenyl)sulfonyl]amino]-2-hexene (11). A. From Adduct 4.** Phenylmagnesium bromide (3 M in ether, 1.0 mL, 3.0 mmol) was added to a solution of adduct **4** (0.226 g, 0.5 mmol) in dry THF (40 mL) at −60 °C under nitrogen with stirring. After being stirred for 1.5 h at −60 °C, the mixture was treated with saturated NH_4Cl solution and was extracted with ethyl acetate. The extract was washed with water and dried (Na_2SO_4), and the solvent was evaporated. To the residue were added methanol (20 mL) and trimethyl phosphite (0.09 mL, 0.75 mmol), and the solution was refluxed for 0.5 h. The solvent was evaporated, and the residue was purified by chromatography on silica gel eluting with hexane–ethyl acetate (1:1) to give **11** as colorless crystals (0.175 g, 83%). Recrystallization of **11** from ethyl acetate–ether gave colorless prisms: mp 157–159 °C; IR (Nujol) 3250, 1320, 1160, 1090, 1070, 1040, 960, 890, 810, 670 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 0.95 (3 H, d, J = 6.7 Hz), 1.40 (3 H, d, J = 6.3 Hz), 2.41 (3 H, s), 2.43 (3 H, s), 3.31 (1 H, m), 3.51 (1 H, m), 4.80 (1 H, d, J = 8.4 Hz) 4.90 (1 H, d, J = 7.5 Hz), 5.03 (1 H, dd, J = 7.9, 15.4 Hz), 5.19 (1 H, dq, J = 6.3, 15.4 Hz), 7.2–7.8 (8 H, m); CI MS 423 ((M + 1)/z). Anal. Calcd for $C_{20}H_{26}N_2O_4S_2$: C, 56.84; H, 6.20. Found: C, 56.71; H, 6.21.

B. From Adduct 3. Methyllithium (1.35 M in ether, 0.37 mL, 0.5 mmol) was added to a solution of adduct **3** (0.090 g, 0.2 mmol) in dry THF (12 mL) at −60 °C under nitrogen with stirring. After being stirred for 1.5 h at −60 °C the mixture was treated with saturated NH_4Cl solution and was extracted with ethyl acetate. The extract was washed with water and dried (Na_2SO_4), and the solvent was evaporated. To the residue were added methanol (8 mL) and trimethyl phosphite (0.04 mL, 0.33 mmol), and the solution was refluxed for 0.5 h. The solvent was evaporated, and the residue was purified by chromatography on silica gel eluting with hexane–ethyl acetate (1:1) to give **11** as colorless crystals (0.060 g, 71%) identical with material obtained in A.

Methyl (±)-[*R,*R**-(*E*)]-[1-[1-(Methoxycarbonyl)aminoethyl]-2-butenyl]carbamate (12).** Reaction of adduct **6** by the procedure described for the preparation of **11**, using phenylmagnesium bromide (1.2 equiv) and trimethyl phosphite (2.0 equiv), gave **12** as colorless crystals (92%): mp 118–120 °C (ethyl acetate–ether); IR (Nujol) 3325, 1690, 1380, 1340, 1300, 1280, 1200, 1100, 1060, 1020, 960, 920, 780, 720, cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.15 (3 H, d, J = 6.7 Hz), 1.70 (3 H, dd, J = 0.8, 6.4 Hz), 3.67 (6 H, s), 3.74 (1 H, m), 3.99 (1 H, m), 4.96 (1 H, m), 5.17 (1 H, m), 5.34 (1 H, ddq, J = 0.8, 7.2, 15.0 Hz), 5.71 (1 H, dq, J = 6.2, 15.0 Hz); CI MS 231 (M + 1/z). Anal. Calcd for $C_{10}H_{18}N_2O_4$: C, 52.16; H, 7.88. Found: C, 52.21; H, 7.80.

(±)-[4α,5β(*E*)]-4-Methyl-5-(1-propenyl)-2-imidazolidinone (13). A mixture of vicinal carbamate **12** (46 mg, 0.20 mmol), NaH (50% in mineral oil, 20 mg, 0.43 mmol), and dry THF (14 mL) was stirred at room temperature for 1 h. The solvent was evaporated, and the residue was dissolved in methanol (6 mL). To this solution was added 1 N NaOH (1.1 mL), and the mixture was stirred at room temperature for 4 h. The solvent was evaporated, and the residue was partitioned between ethyl acetate and water. The organic layer was washed with water and dried (Na_2SO_4). and the solvent was evaporated. The residue was purified by chromatography on silica gel eluting with ethyl acetate to give imidazolidinone **13** as colorless crystals (24 mg, 86%). Recrystallization of **13** from ethyl acetate gave colorless needles: mp 166–167 °C; IR (Nujol) 3200, 1710, 1570, 1330, 1220, 970, 750 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.22 (3 H, d, J = 6.1 Hz), 1.70 (3 H, dd, J = 1.4, 6.4 Hz), 1.97 (1 H, m), 3.71 (1 H, t, J = 7.6 Hz), 5.1 (1 H, br), 5.3 (1 H, br), 5.43 (1 H, ddq, J = 1.4, 7.7, 15.2 Hz), 5.68 (1 H, dq, J = 6.4, 15.2 Hz); mass spectrum, m/z (relative intensity) 140 [M$^+$] (18.0), 125 (2.9), 111 (1.5), 99 (8.9), 82 (4.0), 70 (6.8), 56 (5.1), 44 (100.0), 28 (77.0). High-resolution mass spectrum calcd for $C_7H_{12}N_2O$: 140.0950. Found, 140.0949.

Methyl (±)-[*R,*R**-(*E*)]-[1-[1-(Methoxycarbonyl)amino]ethyl]-2-butenyl]-*N*-phenylthiocarbamate (17).** Phenylmagnesium bromide (3 M in ether, 0.11 mL, 0.33 mmol) was added to a solution of adduct **6** (70 mg, 0.27 mmol) in dry THF (5 mL) at −60 °C under nitrogen with stirring. After being stirred for 20 min at −60 °C, the mixture was treated with saturated NH_4Cl solution and was extracted with ethyl acetate. The extract was washed with water and dried (Na_2SO_4), and the solvent was evaporated. The residue was purified by column chromatography on silica gel eluting with hexane–ethyl acetate (3:2) to give **17** as colorless crystals (84 mg, 92%). Recrystallization of **17** from ether–hexane gave colorless prisms: mp 93–95 °C; IR (Nujol) 3350, 1710, 1690, 1640, 1320, 1280, 1250, 1040, 960, 760, 740, 690 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.10 (3 H, d, J = 6.6 Hz), 1.51 (3 H, d, J = 6.2 Hz), 3.61 (3 H, s), 3.80 (3 H, s), 3.99 (1 H, m), 4.61 (1 H, t, J = 9.3 Hz), 4.81 (1 H, m), 5.47 (1 H, dd, J = 8.8, 15.3 Hz), 5.72 (1 H, dq, J = 6.2, 15.3 Hz), 7.1–7.3 (5 H, m); CI MS 339 ((M + 1)/z). Anal. Calcd for $C_{16}H_{22}N_2O_4S$: C, 56.78; H, 6.55. Found: C, 56.71; H, 6.64.

(±)-[*R,*S**-(*E*)]-4,5-Bis[[(4-methylphenyl)sulfonyl]amino]-2-hexene (18).** Conversion of **7** by the procedure described for the preparation of **11** from **4** using phenylmagnesium bromide (9.0 equiv), trimethyl phosphite (1.5 equiv), and (*E*)-erythro-vicinal sulfonamide gave **18** as colorless crystals (71%). Recrystallization of **18** from ethyl acetate–ether gave colorless prisms: mp 174–175 °C; IR (Nujol) 3250, 1135, 1160, 1090, 1070, 1040, 960, 900, 810, 670 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 0.86 (3 H, d, J = 6.8 Hz), 1.47 (3 H, d, J = 6.8 Hz), 2.42 (3 H, s), 2.44 (3 H, s), 3.27 (1 H, m), 3.57 (1 H, m), 4.79 (1 H, d, J = 9.1 Hz), 5.09 (1 H, dd, J = 7.2, 15.2 Hz), 5.19 (1 H, d, J = 8.7 Hz), 5.32 (1 H, dq, J = 6.8, 15.2 Hz), 7.2–7.7 (8 H, m); CI MS 423 ((M + 1)/z). Anal. Calcd for $C_{20}H_{26}N_2O_4S_2$: C, 56.84; H, 6.20. Found: C, 56.84; H, 6.14.

Methyl (±)-[*R,*S**(*E*)]-[1-[1-[(Methoxycarbonyl)amino]ethyl]-2-butenyl]carbamate (19). A.** Reaction of **10** with methyllithium (2.4 equiv) and trimethyl phosphite (2.0 equiv) by the procedure described for the preparation of **11** from **3** gave **19** as colorless crystals (38%): mp 151–153 °C (ethyl acetate–hexane); IR (Nujol) 3340, 1690, 1380, 1330, 1300, 1240, 1200, 1020, 970, 780, 720 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.13 (3 H, d, J = 6.6 Hz), 1.74 (3 H, dd, J = 1.3, 6.4 Hz), 3.69 (6 H, s), 3.91 (1 H, m), 4.19 (1 H, m), 4.83 (1 H, br), 5.4 (2 H, m), 5.71 (1 H, dq, J = 6.6, 15.3 Hz); CI MS 231 ((M + 1)/z). Anal. Calcd for $C_{10}H_{18}N_2O_4$: C, 52.16; H, 7.88. Found: C, 52.06; H, 7.71.

B. The (*E*)-erythro vicinal carbamate **19** identical with that prepared in A was obtained in 94% yield from the adduct **9** by reaction with phenylmagnesium bromide (2.0 equiv) followed by desulfurization with trimethyl phosphite (2.0 equiv) as described for preparation of **11** from adduct **4**.

(±)-[4α,5α(*E*)]-4-Methyl-5-(1-propenyl)-2-imidazolidinone (20). The imidazolidinone **20** was prepared in 83% yield from **19** by the procedure described for the preparation of **13** from **12**. Recrystallization of **20** from ethyl acetate gave colorless prisms: mp 170–171 °C; IR (Nujol) 3200, 1710, 1570, 1260, 970, 720 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.10 (3 H, d, J = 6.5 Hz), 1.73 (3 H, dd, J = 1.5, 6.3 Hz), 3.89 (1 H, dq, J = 6.5, 7.2 Hz), 4.18 (1 H, t, J = 8.0 Hz), 4.8 (1 H, br), 5.0 (1 H, b), 5.47 (1 H, ddq, J = 1.5, 8.0, 15.2 Hz), 5.69 (1 H, dq, J = 6.5, 15.2 Hz); mass spectrum, m/z (relative intensity) 140 [M$^+$] (18.8), 125 (3.8), 111 (1.7), 98 (2.9), 82 (3.6), 70 (6.6), 56 (2.7), 44 (100.0), 28 (16.2). High resolution mass spectrum calcd for $C_7H_{12}N_2O$: 140.0950. Found: 140.0947.

Dimethyl (±)-[3α,4α(*E*)]-3-Methyl-4-(1-propenyl)-1,2,5-thiadiazolidine-2,5-dicarboxylate (24). A solution of adduct **10** (80 mg, 0.33 mmol) in 8 mL of dry benzene was refluxed under nitrogen for 1 h. The solvent was evaporated, and the residue was purified by column chromatography on silica gel eluting with hexane–ethyl acetate (3:1) to give thiadiazolidine **24** as a colorless oil (77 mg, 96%): IR (film) 1720, 1440, 1330, 1260, 1200, 1120, 1070, 970, 760 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.26 (3 H, d, J = 6.7 Hz), 1.75 (3 H, dd, J = 1.4, 6.5 Hz), 3.74 (3 H, s), 3.76 (3 H, s), 4.67 (1 H, dq, J = 6.7, 7.5 Hz), 4.87 (1 H, dd, J = 7.5, 8.4 Hz), 5.52 (1 H, ddq, J = 1.4, 8.4, 15.2 Hz), 5.79 (1 H, dq, J = 6.5, 15.2 Hz); mass spectrum, m/z (relative intensity) 260 [M$^+$] (35.4), 144 (100.0), 100 (31.1), 82 (17.9), 67 (16.7), 59 (30.8).

The following thiadiazolidines were prepared by using the above procedure:

Dimethyl (±)-[3α,4β(*E*)]-3-methyl-4-(1-propenyl)-1,2,5-thiadiazolidine-2,5-dicarboxylate (22): from **5** in 96% yield; colorless oil; IR (film)

1700, 1440, 1350, 1280, 1200, 1100, 960, 760 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.31 (3 H, d, J = 6.6 Hz), 1.69 (3 H, dd, J = 1.3, 6.4 Hz), 3.75 (3 H, s), 3.77 (3 H, s), 4.48 (1 H, q, J = 6.6 Hz), 4.52 (1 H, d, J = 6.2 Hz), 5.41 (1 H, ddq, J = 1.3, 6.2, 15.2 Hz), 5.74 (1 H, dq, J = 6.4, 15.2 Hz); mass spectrum, m/z (relative intensity) 260 [M$^+$] (41.9), 144 (100.0), 100 (31.6), 82 (24.3), 67 (18.6), 59 (33.5).

(±)-[3α,4β(*E*)]-2,5-Bis[(4-methylphenyl)sulfonyl]-3-methyl-4-(1-propenyl)-1,2,5-thiadiazolidine (21): from **3** in 100% yield; colorless oil; IR (film) 1600, 1440, 1340, 1160, 1090, 820, 760 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.28 (3 H, d, J = 6.1 Hz), 1.50 (3 H, dd, J = 1.6, 6.5 Hz), 2.42 (3 H, s), 2.46 (3 H, s), 3.71 (2 H, m), 4.95 (1 H, m), 5.55 (1 H, dq, J = 6.5, 15.3 Hz), 7.2–7.9 (8 H, m); mass spectrum, m/z (relative intensity) 452 [M$^+$] (2.5), 297 (40.1), 224 (3.8), 198 (4.1), 155 (35.8), 141 (14.4), 126 (9.0), 100 (31.3), 91 (100.0).

(±)-[3α,4α(*E*)]-2,5-Bis[(4-methylphenyl)sulfonyl]-3-methyl-4-(1-propenyl)-1,2,5-thiadiazolidine (23). A suspension of an inseparable 1:1 mixture of adducts **7** and **8** (50 mg) in 6 mL of dry benzene was refluxed for 1.5 h under nitrogen, during which time the mixture dissolved. The solution was concentrated, and adduct **7** separated as colorless crystals (20 mg). The filtrate was evaporated, and the residue was purified by column chromatography on silica gel eluting with hexane–ethyl acetate (3:1) to give **23** as a colorless oil (23.7 mg, 95% based on adduct **8**; adduct **7** was recovered unchanged): IR (film) 1600, 1440, 1340, 1160, 1080, 820, 760 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.24 (3 H, d, J = 6.7 Hz), 1.64 (3 H, d, J = 5.1 Hz), 2.43 (6 H, s), 4.09 (1 H, m) 4.24 (1 H, m), 5.47 (2 H, m), 7.2–7.8 (8 H, m); mass spectrum, m/z (relative intensity) 452 [M$^+$] (1.4), 297 (45.5), 224 (3.9), 198 (4.2), 155 (40.0), 141 (13.0), 126 (7.5), 100 (28.0), 91 (100.0).

Dimethyl (±)-[3α,4β(*Z*)]-3-Methyl-4-(1-propenyl)-1,2,5-thiadiazolidine-2,5-dicarboxylate (25). A mixture of adduct **9** (120 mg, 0.46 mmol) and 36 mL of dry toluene was refluxed under nitrogen for 7 h. The solvent was evaporated, and the residue was chromatographed on silica gel using hexane–ethyl acetate (4:1) as eluant to give thiadiazolidine **25** as a colorless oil (33 mg, 28%): IR (film) 1720, 1440, 1360–1260, 1200, 1100, 1060, 760 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.33 (3 H, d, J = 6.6 Hz), 1.78 (3 H, dd, J = 1.8, 7.0 Hz), 3.77 (6 H, s), 4.33 (1 H, q, J = 6.6 Hz), 4.94 (1 H, d, J = 8.7 Hz), 5.41 (1 H, ddq, J = 1.8, 8.7, 10.1 Hz), 5.69 (1 H, dq, J = 7.0, 10.1 Hz); mass spectrum, m/z (relative intensity) 260 [M$^+$] (31.8), 144 (100.0), 100 (36.7), 82 (20.6), 67 (24.6), 59 (35.8).

Reduction of Thiadiazolidines with Sodium Borohydride. To a solution of **22** (52 mg, 0.2 mmol) in methanol (5 mL) was added sodium borohydride (43 mg, 1.1 mmol) at room temperature with stirring, and the mixture was stirred for 15 min at room temperature. The solvent was evaporated, and $CHCl_3$ was added to the residue. The mixture was washed with aqueous NaCl and dried (Na_2SO_4). The solvent was evaporated, and the residue was purified by chromatography on silica gel eluting with hexane–ethyl acetate (2:1) to give **12** (42 mg, 91%) as colorless crystals, mp 118–120 °C, having IR and ^{1}H NMR spectra identical with those of material obtained from adduct **6** by reaction with phenylmagnesium bromide and trimethyl phosphite.

Other vicinal diamine derivatives prepared by this method from the corresponding thiadiazolidines were as follows: **11**, 94% from **21**; **18**, 72% from **23**; **19**, 91% from **24**.

Reduction of thiadiazolidine **25** as above gave methyl (±)-[*R**,*R**(*Z*)]-[1-[1-[(methoxycarbonyl)amino]ethyl]-2-butenyl]carbamate (**26**): colorless oil (95%); IR (film) 3340, 1730–1690, 1530, 1450, 1250, 1100–1030, 780, 750 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.14 (3 H, d, J = 6.7 Hz), 1.73 (3 H, dd, J = 1.7, 6.9 Hz), 3.67 (6 H, s), 3.73 (1 H, m), 4.33 (1 H, dd, J = 8.9, 17.3 Hz), 4.88–5.04 (2 H, br), 5.25 (1 H, ddq, J = 1.7, 8.9, 10.1 Hz), 5.71 (1 H, dq, J = 6.7, 10.1 Hz); CI MS 231 ((M + 1)/z).

Methyl (±)-(*R,*R**)-[1-[1-[(Methoxycarbonyl)amino]ethyl]butyl]carbamate (27). A. Hydrogenation of 26.** A mixture of **26** (30 mg, 0.13 mmol), $PtO_2 \cdot H_2O$ (15 mg), and ethyl acetate (4 mL) was stirred under 1 atm of hydrogen at room temperature for 2 h. The mixture was filtered, and the filtrate was evaporated to give **27** as a colorless oil (22 mg, 73%) which was essentially pure as evidenced by ^{1}H NMR and TLC: IR (film) 3350, 2960, 1730–1690, 1530, 1460, 1250, 1200, 1110, 1080, 1050, 1040, 780 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.91 (3 H, t, J = 6.9 Hz), 1.17 (3 H, d, J = 6.6 Hz), 1.26–1.53 (4 H, m), 3.66 (6 H, s), 3.5–3.7 (2 H, m), 5.1–5.2 (2 H, m); CI MS 233 ((M + 1)/z).

B. Hydrogenation of 12. As described above, **12** (17 mg, 0.07 mmol) was hydrogenated over $PtO_2 \cdot H_2O$ (25 mg) in ethyl acetate for 3 h to give **27** as a colorless oil (12 mg, 71%), having TLC, IR, ^{1}H NMR, and CI mass spectra identical with those of material obtained in A.

Reaction of Bis(imide) 1b with Cyclohexadiene. To a solution of bis(imide) **1b** (0.210 g, 1.1 mmol) in dry benzene (6 mL) was added 1,3-cyclohexadiene (**28**, 0.156 mL, 1.6 mmol) at room temperature with stirring. The mixture was stirred for 14 h at room temperature, and the solvent was evaporated. The residue was chromatographed on silica gel. Elution with hexane–ethyl acetate (5:1, followed by 3:1) gave the thiadiazolidine **30** as a colorless oil (0.087 g, 29%) and the aminocyclohexadiene derivative **31** as a colorless oil (0.024 g, 8%). Further elution with ethyl acetate gave the Diels–Alder adduct **29** as a colorless oil (0.127 g, 42%).

Data for 30: IR (film) 1710, 1440, 1350–1250, 1120, 1030, 980, 960, 920, 890, 790, 760, 730 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.73–2.28 (4 H, m), 3.77 (3 H, s), 3.78 (3 H, s), 4.50 (1 H, m), 4.99 (1 H, m), 5.71 (1 H, m), 6.13 (1 H, m); mass spectrum, m/z (relative intensity) 258 [M$^+$] (100.0), 148 (18.3), 120 (10.9), 90 (48.6), 80 (65.7), 79 (61.0), 59 (48.4), 49 (36.9).

Data for 29: IR (film) 1720, 1660, 1440, 1370, 1300, 1230, 1050, 940, 870, 750 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.62 (2 H, m), 2.40 (1 H, m), 3.20 (1 H, m), 3.72 (3 H, s), 3.81 (3 H, m), 4.02 (1 H, m), 5.05 (1 H, m), 6.47 (1 H, m), 6.90 (1 H, m); mass spectrum, m/z (relative intensity) 258 [M$^+$] (9.4), 180 (14.2), 148 (4.1), 120 (15.6), 90 (70.2), 79 (100), 67 (16.5), 59 (41.3), 47 (15.0), 41 (16.7).

Data for 31: IR (film) 3300, 1720, 1440, 1280, 1210, 1060, 950, 850, 780 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.41–2.76 (2 H, m), 3.76 (3 H, s), 3.83 (3 H, s), 4.98–5.11 (1 H, m), 5.63–5.70 (1 H, m), 5.84–6.12 (1 H, m), 6.63 (1 H, NH); CI MS 259 ((M + 1)/z).

(±)-5-[(Methoxycarbonyl)amino]-1,3-cyclohexadiene (32). To a solution of **31** (30 mg, 0.12 mmol) in methanol (4 mL) was added sodium borohydride (40 mg, 1.1 mmol) at room temperature with stirring, and the mixture was stirred for 15 min at room temperature. Workup as described for the sodium borohydride reduction of **22** gave **32** as a colorless oil (14 mg, 79%): IR (film) 3340, 1710, 1530, 1250, 1050, 780 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.33–2.49 (2 H, m), 3.65 (3 H, s), 4.30–4.36 (1 H, m), 4.85–4.87 (1 H, NH), 5.77–6.08 (4 H, m); mass spectrum, m/z (relative intensity) 153 [M$^+$] (22.7), 120 (20.2), 94 (10.6), 78 (100), 67 (15.9), 59 (11.6), 51 (7.6), 39 (15.1), 28 (18.1). High-resolution mass spectrum calcd for $C_8H_{11}NO_2$: 153.0790. Found: 153.0781.

(±)-*cis*-3,4-Bis[(methoxycarbonyl)amino]cyclohexene (33). A. Prepared from Diels–Alder adduct **29** in 85% yield using phenylmagnesium bromide (1.2 equiv) and methanolic trimethyl phosphite as described above for conversion of **4** to **11**: colorless prisms from ether: mp 110–111 °C; IR (Nujol) 3375, 3350, 1720, 1685, 1260, 1240, 1060, 1040, 780 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.60 (1 H, m), 1.88 (1 H, m), 2.15 (2 H, m), 3.68 (3 H, s), 3.69 (3 H, s), 3.94 (1 H, m), 4.36 (1 H, m), 4.72 (1 H, m), 5.61 (1 H, m), 5.81 (1 H, m), 5.86 (1 H, m); CI MS 229 ((M + 1)/z).

B. Sodium borohydride reduction of thiadiazolidine **30** as described for reduction of **22** and **12** gave **33** in 91% yield identical with the material prepared in A.

Acknowledgment. We thank the National Science Foundation for support of this research (CHE-81-00132) and Takeda Chemical Industries, Ltd. for a research fellowship to H. N. S.M.W. is grateful to the John Simon Guggenheim Memorial Foundation for a Fellowship (1983–84). Helpful discussions with R. Garigipati are also acknowledged.

Registry No. 1a, 851-06-9; **1b**, 16762-82-6; (±)-**3**, 93133-33-6; (±)-**4**, 93133-34-7; (±)-**5**, 93061-98-4; (±)-**6**, 93133-35-8; (±)-**7**, 93133-36-9; (±)-**8**, 93133-37-0; (±)-**9**, 93133-38-1; (±)-**10**, 93133-39-2; (±)-**11**, 93084-46-9; (±)-**12**, 93061-99-5; (±)-**13**, 93062-00-1; (±)-**15**, 93062-13-6; (±)-**17**, 93062-01-2; (±)-**18**, 93062-02-3; (±)-**19**, 93062-03-4; (±)-**20**, 93133-40-5; (±)-**21**, 93062-04-5; (±)-**22**, 93062-05-6; (±)-**23**, 93133-41-6; (±)-**24**, 93133-42-7; (±)-**25**, 93133-43-8; (±)-**26**, 93062-06-7; (±)-**27**, 93062-07-8; **28**, 592-57-4; (±)-**29**, 93062-08-9; (±)-**30**, 93062-09-0; (±)-**31**, 93062-10-3; (±)-**32**, 93062-11-4; (±)-**33**, 93062-12-5; Ts—N=S=O, 4104-47-6; $(MeO)_3P$, 121-45-9; PhMgBr, 100-58-3; MeLi, 917-54-4; (*E*,*E*)-2,4-hexadiene, 5194-51-4; (*E*,*Z*)-2,4-hexadiene, 5194-50-3.

Supplementary Material Available: Complete X-ray for adducts **3** and **7** (22 pages). Ordering information is given on any current masthead page.