# Reactivity and Diastereoselectivity in the Thermal and Lewis Acid−Catalyzed Diels−Alder Reactions of N -Sulfinylphosphoramidates 1

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## Reactivity and Diastereoselectivity in the Thermal and Lewis Acid-Catalyzed Diels−Alder Reactions of *N*-Sulfinylphosphoramidates[1]

Yinsheng Zhang*,† and Christopher J. Flann*,‡

*Department of Chemistry, University of Montana, Missoula, Montana 59812*

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The [4 + 2] cycloaddition reactions of *N*-sulfinylphosphoramidates, prepared from the corresponding phosphoramidates by treatment with *N*-(chlorosulfinyl)imidazole, and 1,3-cyclohexadiene were found to be diastereoselective in the absence (>90:10) and presence (>95:5) of Lewis acid. The sulfur configuration of the major adduct from the cycloaddition reaction has been established unambiguously by X-ray crystallography. The use of Lewis acids improved the diastereoselectivity and yield, as well as shortened reaction times. Based on the intermediacy of a tin chelate, and the absence of phosphoryl secondary orbital interactions, a mechanism for the cycloaddition reactions is discussed.

### Introduction

The Diels−Alder chemistry of phosphoryl activated *N*-sulfinyl compounds had previously seen little research. In 1963, Wieczorkowski[2] reported the first example of a Diels−Alder reaction between diethyl *N*-sulfinylphosphoramidate (G = P(O)(OEt)$_2$) and a 1,3-diene to afford a 3,6-dihydro-2*H*-1,2-thiazine 1-oxide (eq 1). Subsequent studies, notably by Kataev and Bal'on, showed that this dienophile exhibited reasonable levels of reactivity and


G = $SO_2Ar$; $CO_2R$; $SONR_2$; $P(O)R_2$; Ar; etc.

regioselectivity with various dienes.[3,4] These isolated reports represent the extent of research in this area. This dearth of studies on the phosphoryl variant of Diels−Alder reactions featuring *N*-sulfinyl dienophiles (eq 1) stands in stark contrast to the many studies in which the sulfonamide (G = $SO_2$Ph) and the carbamate (G = COOR) serve as the activating group.[5a−c]

As part of our interest in the development of new methodology for asymmetric synthesis via homochiral organophosphorus compounds,[6] we undertook a systematic study of the [4 + 2] cycloaddition of *N*-sulfinylphosphoramidates **3a**−**f** with various dienes. The reactivity and diastereoselectivity of this [4 + 2] cycloaddition in the absence and presence of a Lewis acid is reported herein.

### Results

**Preparation of *N*-Sulfinylphosphoramidates 3a−f.** The *N*-sulfinyl compounds are usually prepared from their corresponding amides.[5c] Phosphoramidates **2a**−**c** were prepared in good yield by the reaction of phosphorines **1a**−**c** (commercially available) with $CCl_4$ and $NH_3$ gas at room temperature.[7] Cyclic phosphoramidates **2d**−**f** were obtained in high yield from the treatment of corresponding chlorides **1d**−**f** with $NH_3$ gas in benzene.

Little is known about *N*-sulfinylphosphoramidates, but the preparation of other *N*-sulfinyl compounds has been investigated.[5c] Compounds **3a**−**c** were readily prepared by the reaction of amides **2a**−**c** with $SOCl_2$ in the absence or presence of pyridine. The acid sensitivity of compounds **3d**−**f** suggested that modification of this method by addition of tertiary amine bases, such as pyridine and triethylamine, might be beneficial. However, such modification provided very poor yields of *N*-sulfinylphosphoramidates **3d**−**f** (25% to 40%).

The substitution of *N*-(chlorosulfinyl)imidazole for $SOCl_2$, however, afforded the desired compounds **3a**−**f** in good yields. *N*-(Chlorosulfinyl)imidazole,[8] formed by a direct treatment of imidazole with excess thionyl chloride, was used in situ for the synthesis of the *N*-sulfinylphosphoramidates **3a**−**f**.

† Current address: Le Research, Inc., 2715 Upper Afton Road, St. Paul, MN 55119.

‡ Current address: Moulton, Bellingham, Longo & Mather, P. C., 1900 Sheraton Plaza, P.O. Box 2559, Billings, MT 59103-2559.

(1) Presented at the 47th Northwest Regional Meeting of ACS, Missoula, MT, 1992, ORGN 116.

(2) Wieczorkowski, J. *Chem. Ind.* **1963**, 825.

(3) Kataev, E. G.; Plemenkov, V. V.; Markin, V. V. *Dokl. Akad. Nauk. SSSR* **1965**, *165*, 1313.

(4) Levchenko, E. S.; Bal'on, Ya G.; Kirsanov, A. V. *Zh. Org. Khim.* **1967**, *30*, 1883.

(5) These reactions have been widely investigated from a synthetic and mechanistic perspective. For comprehensive reviews see: (a) Weinreb, S. M. *Acc. Chem. Res.* **1988**, *21*, 313. (b) Boger, D. L.; Weinreb, S. M. In *Hetero Diels−Alder Methodology in Organic Synthesis*; Academic: San Diego, 1987; p 1. (c) Bussas, P.; Kresze, G.; Munsterer, H.; Schwobel, A. *Sulf. Rep.* **1983**, *2*, 215.

(6) Flann, C. J. *Book of Abstracts*; ACS 32nd National Organic Chemistry Symposium, American Chemical Society: Washington, DC, 1991, p 288.

(7) Atherton, F. R.; Openshaw, T. H.; Todd, A. R. *J. Org. Chem.* **1945**, 663.

(8) Kim, Y. H.; Shin, J. M. *Tetrahedron Lett.* **1985**, *26*, 3821.

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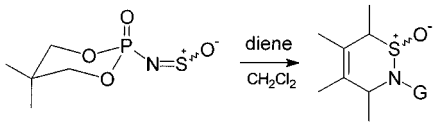
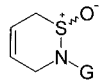
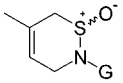
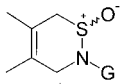
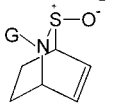
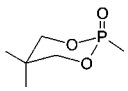
**Table 1. Cycloadditions of *N*-Sulfinylphosphoramidate 3d and Dienes**




3d 4d-7d

| Entry | Dienes | Reaction time (h) | Adducts | Yields[a] |
|---|---|---|---|---|
| 1 |  | 10 |  **4d** | 40% |
| 2 |  | 4 |  **5d** | 52% |
| 3 |  | 4 |  **6d** | 65% |
| 4 |  | 6 |  **7d** | 45% |

[a] Yields are based on phosphoramidate **2d**. G= 

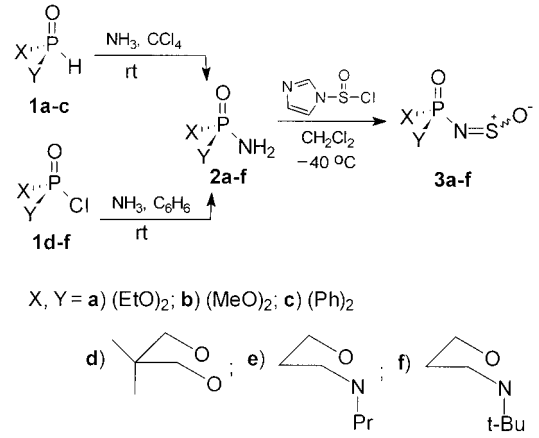
Compounds **3a** and **3b** were purified by distillation. Thermally unstable and moisture sensitive compounds **3c**−**f** were used as formed in situ.

**Reactivity of *N*-Sulfinylphosphoramidates in [4 + 2] Cycloadditions.** The previous studies indicated these compounds underwent the [4 + 2] cycloaddition reaction, but under conditions suggesting low dieneophile reactivity.[2−4] Wieczorkowski reported that diethyl *N*-sulfinylphosphoramidate **3a** only reacted with dienes at 60−70 °C in benzene.[2] However, we found the cycloaddition of compounds **3a**−**f** took place at room temperature in $CH_2Cl_2$ in fair to good yields. The examples of [4 + 2] cycloaddition reactions of compound **3d** with various dienes are shown in Table 1.

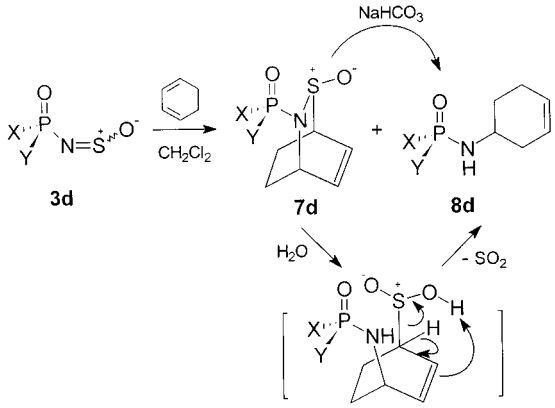
In addition to cycloaddition adducts, phosphoramides were also formed. If compound **3d** was generated without purification, a cycloaddition reaction with cyclohexadiene afforded the desired adduct **7d** and a byproduct which has been identified as **8d** based on $^1$H, $^{13}$C, $^{31}$P NMR and elemental analysis. This same product was obtained by the treatment of adduct **7d** with HCl or caustic soda,[4] indicating that the byproduct was formed from the adduct **7d** by loss of $SO_2$ (Scheme 2). These results illustrate that the adducts can be readily converted to $\beta$-aminoalkenes **8d**.

The dienophiles showed reactivity with a broad range of dienes. The relatively unreactive butadiene provides an adduct in good yield, while the most reactive diene, cyclopentadiene, affords a complicated mixture from which **9d** can be isolated. This product appears to result from a [3 + 2] cycloaddition. However, a more reasonable explanation is a [2,3]-sigmatropic rearrangement after the [4 + 2] cycloaddition reaction, as shown in Scheme 3.[10,11]

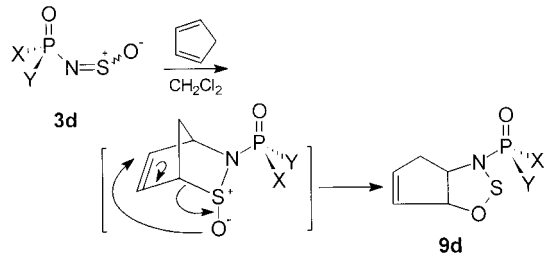
**Scheme 1**




**Scheme 2**




**Scheme 3**




**Regioselectivity and Diastereoselectivity.** Kataev[3] examined the regioselectivity of the cycloaddition of **3a** and 2-substituted 1,3-butadienes and suggested that the major product was a 4-substituted thiazine oxide on the basis of low resolution $^1$H NMR. Later, Bal'on[4] corrected the major product as a 5-substituted thiazine oxide. We also studied the reaction of isoprene with compounds **3a** and **3d** and found only one isomer in each case. Based on the analysis of $^1$H and $^{13}$C NMR, the structures of the adducts are consistent with 5-methylthiazine oxide **5a** (G = $(EtO)_2$) and **5d** (Table 1).

In the cycloaddition reactions of dienes and *N*-sulfinyl compounds, adducts epimeric at sulfur can be formed.

(9) (a) Kashman, Y.; Awerbough, O. *Tetrahedron* **1971**, 5593. (b) Pankiewicz, Z.; Kinas, R.; Stec, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 7712. (c) Cerioni, G.; Piras, P. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1449. (d) McClure, C. K.; Hansen, K. B. *Tetrahedron Lett.* **1996**, *37*, 2049. To our knowledge, the effects of $SnCl_4$ on the chemical shifts of $^{31}$P NMR spectroscopy were not studied before; however, the effects of common chemical shift reagents, such as Eu(dpm)$_3$ and Eu(tfc)$_3$, on the $^{31}$P NMR and Lewis acid $SnCl_4$ on $^1$H and $^{13}$C NMR of carbonyl compounds have been investigated. Our results were consistent with previous reports cited above.

(10) We could not characterize compounds formed in the cycloaddition since they were extremely unstable.

(11) Natsugari, H.; Whittle, R. R.; Weinreb, S. M. *J. Am. Chem. Soc.* **1984**, *106*, 7867.

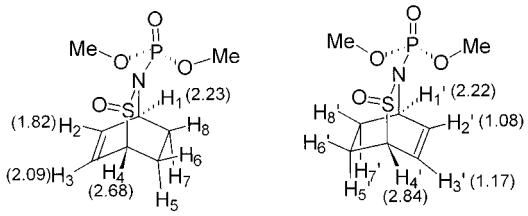


**Figure 1.** Endo/exo sulfur epimers.

Previous studies of these cycloadducts disclose a lack of stereoselectivity at sulfur.[5a] Mock[12] and Weinreb[13] noted the absence of stereoselectivity in the thermal cycloaddition of benzyl *N*-sulfinyl carbamate and *N*-sulfinylbenzenesulfonamide with cyclohexadiene. This apparent general lack of selectivity perhaps precluded development of reactions based on sulfur stereoselectivity or studies to improve or explain the observed selectivity.

In contrast to the *N*-sulfinylcarbamates and -sulfonamides, *N*-sulfinylphosphoramidates **3a**−**f** exhibit great selectivity in the thermal Diels−Alder reaction, providing a >90:10 ratio of sulfur epimers. Furthermore, these isomers were chromatographically separable (**3a** and **3b**). As this new methodology allowed the selective preparation and separation of the sulfur epimers, the configuration of the isomers at sulfur was investigated (Figure 1). Complete NMR spectral information for the two sulfur epimers **7a**, **7a′** and **7b**, **7b′** is given in the Experimental Section.

The spectra of the major and minor isomers show differences in the chemical shifts of $H_{2,3}$ and $H_{5-8}$, which facilitate identification of the stereoisomeric adducts. The chemical shifts of protons $H_{6',8'}$ are particularly affected; protons $H_{6',8'}$ (2.90, 2.31 ppm) in the minor isomer are significantly downfield from those protons $H_{6,8}$ (1.80, 1.75 ppm) in the major isomer. Moreover, the difference of chemical shifts between $H_2$ (6.95 ppm) and $H_3$ (6.28 ppm) in the major isomer ($\Delta\delta = 0.67$ ppm) is larger than that between $H_{2'}$ (6.75 ppm) and $H_{3'}$ (6.29 ppm) in the minor ($\Delta\delta = 0.46$ ppm). Considering the shielding effect of the "S=O" group,[12,14a,b] the assignment of the major isomer as the endo sulfur epimer seems reasonable. $Eu(dpm)_3$ NMR shift experiments supported this hypothesis.[11,13a,b] From the relative magnitude of the induced shift of the respective protons shown in parentheses in Figure 1 (i.e. the slope of a plot of chemical shift vs mole ratio of $Eu(dpm)_3$/sample), the pertinent observation is that the protons $H_{2,3}$ in the major isomer are approximately equally shifted, and both are more strongly affected than the same protons in the minor isomer. In both isomers the bridge head protons ($H_1/H_4$) are similarly strongly shifted. Recognizing the Lewis acidity of $Eu(dpm)_3$ reagent and the strong dipolar characters of both sulfinyl and phosphoryl groups, these induced shifts may indicate a $Eu^{3+}$ complex with the sulfinyl oxygen[12,14a,b] and the phosphoryl oxygen.[9a,b,d] X-ray crystallographic analysis of the major isomer confirmed an endo configuration at sulfur. X-ray crystal structures of **7b** and **7c** are shown in Figure 2.[15]

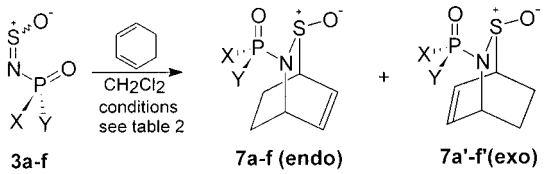
The high selectivity at sulfur observed in the thermal cycloaddition of achiral *N*-sulfinyl compounds **3a**−**d** prompted us to examine the diastereoselectivity derived from phosphorus chiral center through the racemic *N*-sulfinylphosphoramidates **3e** and **3f**. The cycloaddition reactions of **3e** (propyl) and **3f** (*tert*-butyl) with cyclohexadiene provided two endo sulfur epimers[16] (Scheme 5) as major adducts, which were unseparable diastereomers in 56:44 and 69:31 ratio, respectively.

**Table 2. Diastereoselectivity in the Cycloadditions of *N*-Sulfinylphosphoramidates (3a−f)**

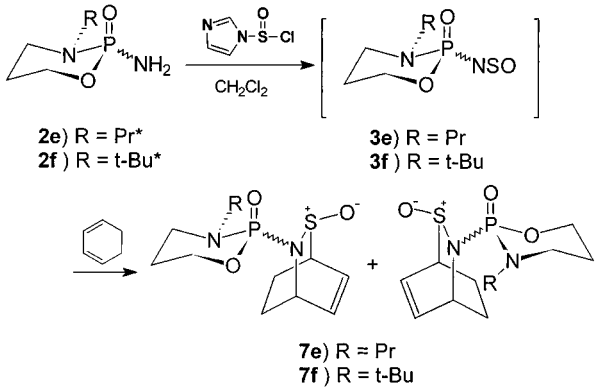
| entry | dienophile | conditions | endo/exo ratio[a] | isolated yield,[b] % |
|---|---|---|---|---|
| 1 | **3a** | 4 h, rt | 91:9 | 74 |
| 2 | | 20 min, $BF_3{\cdot}Et_2O$, rt | >95:5 | 83 |
| 3 | | 15 min, $TiCl_4$, −78 °C | >95:5 | 80 |
| 4 | | 15 min, $SnCl_4$, −78 °C | >95:5 | 90 |
| 5 | | 15 min, $SnCl_4$, 5 °C | >95:5 | 78 |
| 6 | **3b** | 4 h, rt | 92:8 | 78 |
| 7 | | 15 min, $SnCl_4$, −78 °C | >95:5 | 80 |
| 8 | **3c** | 4 h, rt | 90:10 | 50 |
| 9 | | 15 min, $SnCl_4$, −78 °C | >95:5 | 68 |
| 10 | **3d** | 8 h, rt | 93:7 | 45 |
| 11 | | 20 min, $SnCl_4$, −78 °C | >95:5 | 60 |
| 12 | **3e** | 8 h, rt | | 55 |
| 13 | | 20 min, $SnCl_4$, −78 °C | >95:5 | 63 |
| 14 | **3f** | 8 h, rt | | 41 |
| 15 | | 20 min, $SnCl_4$, −78 °C | >95:5 | 55 |

[a] The endo/exo ratio was determined by $^{31}P$ and $^1H$ NMR of the crude. [b] Isolated yields are based on the *N*-phosphoramides **2a**−**f**.

**Scheme 4**




**Scheme 5**




*For simplicity one diastereomer shown only.

**The Effect of Lewis Acids on Stereoselectivity of the Cycloadditions.** Both Weinreb[17] and Whitesell[18] reported the endo/exo selective [4 + 2] cycloaddition of homochiral *N*-sulfinylcarbamates with 1,3-cyclohexadiene and (*E*,*E*)-hexa-2,4-diene in the presence of either

(12) Mock, W. L.; Nugent, R. M. *J. Am. Chem. Soc.* **1975**, *97*, 6521.
(13) Garigipati, R. S.; Cordova, R.; Parvez, M.; Weinreb, S. M. *Tetrahedron* **1986**, *42*, 2979.
(14) (a) Garigipati R. S.; Freyer, A. J.; Whittle, R. R.; Weinreb, S. M. *J. Am. Chem. Soc.* **1984**, *106*, 7861. (b) Bell, S. I.; Parvez, M.; Weinreb, S. M. *J. Org. Chem.* **1991**, *56*, 373.

(15) The author has deposited atomic coordinates for these structures with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2, 1EZ, UK.
(16) The determination of endo sulfur epimers was based on the $^1H$ and $^{13}C$ NMR of known endo sulfur epimers **7a,b,c**. The structure details of these compounds will be published elsewhere.
(17) Remiszewski, S. W.; Yang, J.; Weinreb, S. M. *Tetrahedron Lett.* **1986**, *27*, 1853.

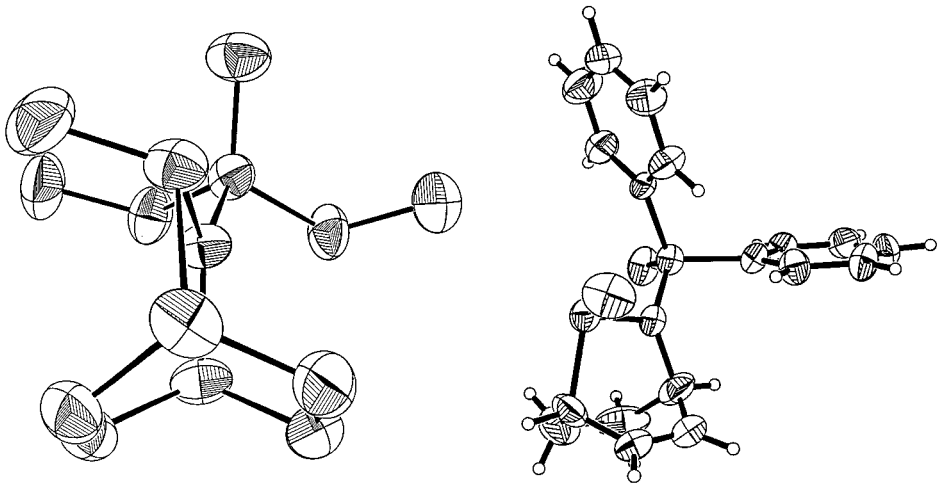


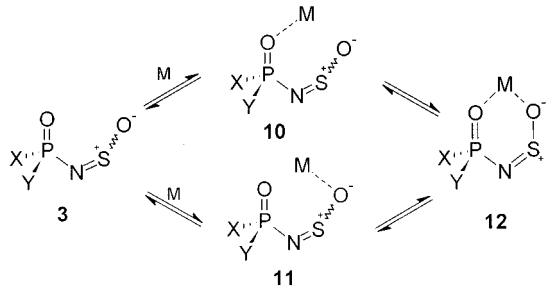
**Figure 2.** X-ray crystal structures of adducts **7b** (X = Y = MeO) and **7c** (X = Y = Ph).

$TiCl_4$ or $SnCl_4$. They noted that Lewis acid plays an important role in asymmetric induction, probably by chelation with *N*-sulfinylcarbamate dienophiles.[17,18] To our knowledge, there are no reports of Lewis acid-catalyzed cycloadditions featuring *N*-sulfinylphosphoramidates. We examined the effect of Lewis acids, such as $BF_3{\cdot}Et_2O$, $SnCl_4$, and $TiCl_4$, on the stereochemistry of the cycloaddition reactions which are shown in Table 2. Lewis acid-catalyzed cycloadditions afforded a single sulfur epimer (based on $^1H$ and $^{31}P$ NMR assay) in high yield. This adduct showed the same configuration at sulfur as the major isomer from the thermal reaction.

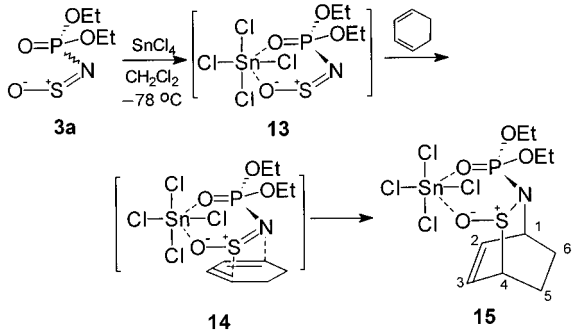
This selectivity extended to reactions involving racemic *N*-sulfinylphosphoramidates **3e** and **3f** and provided additional diastereoselctivity at phosphorus (33:67 and 17:83) over the thermal cycloaddition (Scheme 5).

Lewis acid enhancement of reactivity and stereoselectivity led us to spectroscopically examine the mixtures of Lewis acids and *N*-sulfinylphosphoramides for the evidence of chelates. Due to the presence of Lewis base sites, such as N, S, O, or $\pi$-N=S, in *N*-sulfinylphosphoramidates, several 1:1 and 2:1 solution complexes are theoretically possible. Putative intermediates **10**−**12** should exhibit enhanced electrophilic character, especially intermediate **12**, which features a six-member ring system similar to that proposed by Castellino for the tin chelate of oxazolidinone.[19a] No chelates, **10**−**12**, were ever isolated. However, $^{31}P$ and $^{119}Sn$ NMR study of a mixture of $SnCl_4$ (1 equiv) and compound **3a** showed a change in phosphorus chemical shift from −10.9 ppm to −18.2 ppm,[9b] and a $^{119}Sn$ signal at −1050 ppm.[19b] While not directly supporting chelates such as **10**−**12**, it is worthwhile to note that upon anhydrous workup, the $SnCl_4$-catalyzed cycloaddition of diethyl *N*-sulfinylphosphoramidate (**3a**) with cyclohexadiene produced **15**, a white solid product (Scheme 7), which could also be obtained by adding $SnCl_4$ (1 equiv) to a solution of adduct **7a** (a clear oil) in $CH_2Cl_2$. We were not able to prepare

**Scheme 6**



**Scheme 7**



a single crystal of **15** for unambiguous structure determination. However, based on $^{119}Sn$, $^{13}C$, $^1H$, $^{31}P$ NMR and elemental analysis, a (1:1) $SnCl_4$/adduct chelate with structure **15** is suggested in Scheme 7. Comparison of the $^1H$ NMR spectra of **15** with adduct **7a** showed substantial change in the chemical shifts of all protons, especially alkene protons $H_{2,3}$ and bridgehead protons $H_{1,4}$. These shifts are consistent with proposed structure **15** and are not dissimilar to those seen in the $Eu(dmp)_3$ study of **7a**. The chemical shift differences between $H_2$ and $H_3$, $H_1$ and $H_4$ in **15** are also reduced. A sharp resonance ($^{119}Sn$) at −952 ppm is observed and consistent with a six-coordinate tin species.[19a,b]

## Discussion

Having established the likely operation of a dienophile/Lewis acid chelate as the reactive intermediate in these cycloadditions, the rationale for the observed stereoselectivity can be explored through this hypothesis. For reactions involving *N*-sulfinylcarbamates, Whitesell pro-

(18) Whitesell, J. K.; James, D.; Carpenter, J. F. *J. Chem. Soc., Chem. Commun.* **1985**, 1449. In Whitesell's proposal, the transition states are labeled exo or endo with respect to the carbamate group. In our application of these possible transition states **17**−**20** endo refers to the sulfinyl group.

(19) (a) Castellino, S. *J. Org. Chem.* **1990**, *55*, 5197 and also see references cited there. (b) Wrackmeyer, B. In *Annual Reports on NMR Spectroscopy: $^{119}Sn$ NMR Parameters*; Academic Press: London, 1985; p 73.

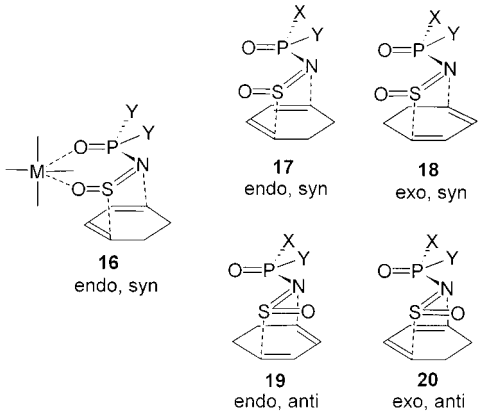



**Figure 3.** [4 + 2] Cycloaddition modes.

posed the scheme illustrated in Figure 3.[18] This proposal recognizes that the endo/exo selectivity and *E*-, *Z*-dienophile stereoisomers can both influence stereoselectivity. The *N*-sulfinylphosphoramidates can correspondingly react with the diene through any one of the four possible cycloaddition modes. However, only two modes, **17** and **19**, can provide the observed stereoselectivity. On the basis of evidence for the presence of a chelate, such as **13**, it seems likely that the cycloaddition proceeds not through the mode exemplified by **19**, but through **17**, enforced through the agency of the Lewis acid as cycloaddition mode **16**.

While the stereoselectivity of the Lewis acid-catalyzed cycloaddition may be readily explained by this model, the operative mode of the thermal reaction is less clear. In the absence of chelation enforcing an endo, syn mode, illustrated by **16**, the predominant stereochemistry is explained equally as well by the endo, anti mode **19** as it is by the endo, syn mode **17**. Regardless of the mode the reaction follows, it is unusual in that the corresponding *N*-sulfinylcarbamate reacts nonstereospecifically. One possible explanation for this phenomena is the absence of a secondary orbital interaction in dienophiles activated by a phosphoryl group. Earlier studies have shown that dienophiles, in which the phosphoryl group is the sole source of activation, are completely nonstereospecific.[20a,b] This lack of secondary orbital interaction stands in stark contrast to that found in dienophiles activated by a carbonyl moiety. This lack of selectivity with *N*-carbamate dienophiles, perhaps, can be explained through conflicting secondary orbital interactions between the carbonyl group and the sulfinyl group. In contrast with the *N*-phosphoryl dienophile, the sulfinyl secondary orbital interactions are not opposed and are perhaps reinforced through steric effects. Whatever the basis for this stereoselection, further studies are planned to elucidate it further by utilizing it in the development of new synthetic methods.

The logic inherent in the above mechanistic proposal can be extended to cycloaddition reactions involving chiral dienophiles. For the achiral dienophiles **3a**−**d**, the reactive intermediate, in either *E* or *Z* form, produces the same sulfur epimer. However, the introduction of chirality in dienophiles **3e,f** creates the possibility that the remote phosphorus chiral center may have a different effect in the different reactive intermediates, **17** and **19**. Indeed, the thermal reaction of **3f** provides a 69:31 mixture of diastereomers at phosphorus, while the Lewis acid-catalyzed reaction provides a 83:17 mixture. The albeit modest extra stereocontrol afforded by the Lewis acid is not readily explained by a reactive intermediate such as **19**; rather, **17** enforced as a cyclic intermediate **16** seems the more likely source of selectivity. Under this analysis, the stereoselectivity at phosphorus results from facial selectivity of the diene reacting in endo mode with a rigid phosphorus chelate. This result and hypothesis suggest that by appropriate manipulation of the environment surrounding phosphorus, the facial selectivity could be improved to synthetically useful levels. Moreover, if the environment surrounding phosphorus that provides the observed stereoselectivity can be prepared from a single chirality, this methodology would be useful for asymmetric synthesis.

(20) (a) Bodalski, R.; Koszak, J.; Krawczyk, H.; Pietrusiewicz, K. M. *J. Org. Chem.* **1982**, *47*, 2219. (b) Daniewski, W. M.; Griffin, C. E. *J. Org. Chem.* **1966**, *31*, 3236.

## Conclusion

In contrast to *N*-sulfinylcarbamates and sulfonamides, the cycloaddition reactions of *N*-sulfinylphosphoramidates and cyclohexadiene showed great diastereoselectivity at sulfur under either thermal (90:10) or Lewis acid (>95:5) conditions. This sulfur stereoselectivity translates into stereoselectivity in the compounds derived from the cycloadducts. A cyclic diene chelate, coupled with the absence of secondary stereoelectronic factors in the dienophile, is proposed to explain this selectivity. We are currently extending these studies to asymmetric cycloadditions by using homochiral *N*-sulfinylphosphoramidates to further test this hypothesis and planning to transform the cycloadducts to useful nitrogen-containing compounds.

## Experimental Section

**General.** All reactions were carried out under an atmosphere of dry nitrogen. Solvents and commercial reagents were used as received without additional purification. $^1$H NMR (270 MHz) and $^{13}$C NMR (90 MHz) spectra were recorded in $CDCl_3$/TMS solutions, unless otherwise stated. $^{31}$P NMR (90 MHz) spectra were recorded in $CDCl_3$ with 85% $H_3PO_4$ as an external standard. Flash chromatography was carried out using 32−63 mm silica gel, and TLC on Merck silica gel plates 60, $S_{254}$. Elemental analyses were performed by the University of Arizona Microanalytic Service Laboratory. Melting points are uncorrected.

**Materials.** Compounds **1a**−**c** were bought from Aldrich Company. **Phosphoramides 2a**−**c** were prepared according to literature.[7] **Diethyl phosphoramidate (2a)**: mp 51−52 °C (lit.[7] 49−50 °C); $^{31}$P NMR $\delta$ 6.5. **Dimethyl phosphoramide (2b)**: bp 98−100 °C/0.5 Torr (lit.[21] bp 98 °C/0.5 Torr); $^{31}$P NMR $\delta$ 12.5; $^1$H NMR $\delta$ 3.69 (d, $J$ = 11.7 Hz, 6H), 3.2 (bs, 2H). ***P,P*-Diphenyl phosphinic amide (2c)**: mp 144−145 °C; $^{31}$P NMR $\delta$ 21.6; $^1$H NMR $\delta$ 7.86−7.94 (m, 5H), 7.41−7.47 (m, 5H), 4.12 (bs, 2H).[4]

**2-Amino-2-oxo-5,5-dimethyl-1,3,2-dioxazaphosphorinan (2d)** was prepared according to literature:[21] mp 126−128 °C (lit.[21] 125−127 °C); $^{31}$P NMR $\delta$ 6.4; $^{13}$C NMR $\delta$ 76.5 (d, $J$ = 6.1 Hz), 32.0 (d, $J$ = 4.9 Hz), 21.6, 20.0. ***N*-Sulfinyl-2-oxo-5,5-dimethyl-1,3,2-dioxazaphosphoramidate (3d)** was generated by adopting Kim's procedure.[8] Yield (crude): 83%; yellow oil; $^1$H NMR $\delta$ 4.20 (m, 2H), 3.95 (m, 2H), 1.35 (s, 3H), 0.92 (s, 3H); $^{13}$C NMR $\delta$ 78.5 (d, $J$ = 9.0 Hz), 32.3 (d, $J$ = 6.1 Hz), 21.8, 20.0; $^{31}$P NMR $\delta$ −13.4.

(21) Zwierzak, A.; Koziara, A. *Tetrahedron* **1970**, *26*, 3521.

**2-Amino-*3*-*n*-propyl-2-oxo-1,3,2-oxazaphosphorinane (2e) and 2-Amino-3-*tert*-butyl-2-oxo-1,3,2-oxazaphosphorinane (2f).** To a cooled (−35 °C) solution of (*N*-alkylamino)-propan-1-ol (3-(*N*-*n*-propylamino)propanol and 3-(*N*-*tert*-butylamino)propanol were synthesized according to Israil's[22a] and Deyrup's[22b] procedures, 23.0 mmol) and triethylamine (48.0 mmol) in $CH_2Cl_2$ (60 mL) was added dropwise a solution of $P(O)Cl_3$ (23.0 mmol) in $CH_2Cl_2$ (15 mL) at −25 to −30 °C. Stirring of the reaction mixture was continued for 2 h at room temperature. Precipitated triethylamine hydrochloride was filtered off, and the filtrate was concentrated. The residual crude product was dissolved in dry $C_6H_6$ (60 mL), and then dry $NH_3$ gas was passed through the reaction mixture at room temperature for 4 h. The crude product **2e** or **2f** was collected by filtration, and pure product was obtained from recrystallization (EtOAc).

**Data for 2e**: white powder; 80% (overall yields); mp 73−75 °C; $^1$H NMR $\delta$ 4.37−4.19 (m, 2H), 3.18−3.05 (m, 2H), 2.98 (bs, 2H), 2.89−2.82 (m, 2H), 1.94−1.87 (m, 2H), 1.59−1.53 (m, 2H), 0.90 (t, $J$ = 7.3 Hz, 3H); $^{13}$C NMR $\delta$ 67.1 (d, $J$ = 7.3 Hz), 49.8, 46.3, 26.4 (d, $J$ = 3.7 Hz), 21.1 (d, $J$ = 4.9 Hz), 11.2; $^{31}$P NMR $\delta$ 13.9; IR (KBr) 3250 (b), 1211(s), 1058(s) cm$^{-1}$. Anal. Calcd for $C_6H_{15}N_2O_2P$: C, 40.43; H, 8.47; N, 15.73. Found: C, 40.74; H, 8.25; N, 15.45.

**Data for 2f**: white powder; 75% (overall yields); mp 100−101 °C; $^1$H NMR $\delta$ 4.35−4.21 (m, 1H), 4.20−4.15 (m, 1H), 3.32−3.19 (m, 1H), 3.17−3.05 (m, 1H), 2.75 (br, 2H), 2.10−1.95 (m, 1H), 1.95−1.85 (m, 1H), 1.38 (s, 9H); $^{13}$C NMR $\delta$ 64.9 (d, $J$ = 7.3 Hz), 54.9 (d, $J$ = 3.7 Hz), 41.7, 29.0 (d, $J$ = 3.7 Hz), 27.3 (d, $J$ = 4.9 Hz); $^{31}$P NMR $\delta$ 9.6; IR (KBr) 3255 (b), 1240 (s), 1106, 1037 (s) cm$^{-1}$. Anal. Calcd for $C_7H_{17}N_2O_2P$: C, 43.72; H, 8.92; N, 14.58. Found: C, 43.88; H, 8.73; N, 14.47.

**Diethyl *N*-Sulfinylphosphoramidate (3a) and Dimethyl *N*-Sulfinylphosphoramidate (3b).** A reaction mixture of dialkyl phosphoramidate (50 mmol), $SOCl_2$ (55 mmol), and anhydrous $C_6H_6$ (25 mL) was heated at 65 °C until the evolution of HCl ceased. The benzene and excess thionyl chloride were distilled off in vacuo. The residue was fractionally distilled. **3a**: yield 70%; bp 85 °C/1.5 Torr (lit.[2] 78%, 77 °C/1 Torr), $^{31}$P NMR $\delta$ −10.9; **3b**: yield 68%; bp 115 °C/2 Torr; $^{31}$P NMR $\delta$ −8.2; $^1$H NMR $\delta$ 3.84 (d, $J$ = 12.0 Hz).

**Thermal Cycloaddition Reactions. Method a: General Procedure for the Preparation of Adducts (5a, 6a, 7a, 7b).** The 1,3-diene (25 mmol) was added dropwise to a solution of freshly distilled dialkyl *N*-sulfinylphosphoramidate (20 mmol) and $CH_2Cl_2$ (25 mL) at 5 °C. The resulting solution was stirred for 3 to 8 h at room temperature. The $CH_2Cl_2$ and excess diene were distilled off in vacuo. The residue consisted of an adduct and a small amount of dialkyl phosphoramidate in the form of a light-yellow liquid which could not be purified further by distillation at 0.05 Torr. Purification of the residue by silica gel column chromatography ($CHCl_3$/$CH_3OH$ or THF/hexane) gave the [4 + 2] adducts as colorless oils or white crystals.

**2-(Diethoxyphosphinyl)-5-methyl-3,6-dihydro-2*H*-1,2-thiazine 1-Oxide (5a).** Oil; 75%; eluting (2% MeOH/$CHCl_3$); $^1$H NMR $\delta$ 5.72 (bs, 1H), 4.30−4.25 (m, 1H), 4.21−4.06 (m, 4H), 3.89 (bd, 1H), 3.54 (bd, 1H, $J$ = 6.5 Hz), 3.16 (bd, 1H, $J$ = 6.5 Hz), 1.84 (s, 3H), 1.42−1.30 (m, 6H); $^{13}$C NMR $\delta$ 122.7, 117.8 (d, $J$ = 7.3 Hz), 63.9 (d, $J$ = 3.7 Hz), 63.5 (d, $J$ = 3.7 Hz), 52.2 (d, $J$ = 4.9 Hz), 37.5, 24.4, 15.8 (d, $J$ = 7.2 Hz); $^{31}$P NMR $\delta$ 2.4; IR (neat) 1255 (s), 1164 (m), 1037 (s) cm$^{-1}$; HRMS calcd for $C_9H_{18}NO_4SP$ 267.0690, found 267.0695.

**2-(Diethoxyphosphinyl)-4,5-dimethyl-3,6-dihydro-2*H*-1,2-thiazine 1-Oxide (6a).** Oil; 80%; eluting (2% MeOH/$CHCl_3$); $^1$H NMR $\delta$ 4.18−4.06 (m, 4H), 3.84 (bd, $J$ = 7.1 Hz, 1H), 3.70−3.62 (m, 1H), 3.47 (bd, $J$ = 6.4 Hz, 1H), 3.10 (bd, $J$ = 6.4 Hz, 1H), 1.79 (s, 3H), 1.76 (s, 3H), 1.36 (t, $J$ = 7.1 Hz, 6H); $^{13}$C NMR $\delta$ 124.4, 115.5, 63.8 (d, $J$ = 3.7 Hz), 63.7 (d, $J$ = 3.7 Hz), 53.7 (d, $J$ = 4.9 Hz), 41.5, 19.9, 17.1, 16.2 (d, $J$ = 6.1 Hz); $^{31}$P NMR $\delta$ 2.3; IR (neat) 1259 (s), 1165, 1134 (m), 1094, 1017 (s) cm$^{-1}$; HRMS calcd for $C_{10}H_{20}NO_4SP$ 281.0846, found 281.0853.

***endo*-3-Aza-*N*-(diethoxylphosphoryl)-2-oxo-2-thiabicyclo[2.2.2]oct-5-ene (7a, major sulfur epimer).** Oil; 68%; eluting (2/5 hex/THF); $^1$H NMR $\delta$ 6.94−6.90 (m, 1H), 6.28 (t, $J$ = 7.4 Hz, 1H), 4.67−4.61 (m, 1H), 4.35−4.32 (m, 1H), 4.21−4.08 (m, 4H), 1.85−1.75 (m, 2H), 1.61−1.52 (m, 1H), 1.35 (t, $J$ = 7.0 Hz, 6H), 1.27−1.15 (m, 1H); $^{13}$C NMR (DMSO-$d_6$) $\delta$ 136.5 (d, $^3J_{P-C}$ = 4.9 Hz), 125.8, 62.6 (d, $^2J_{P-C}$ = 12.2 Hz), 62.8 (d, $J$ = 12.2 Hz), 54.8 (d, $^2J_{P-C}$ = 4.9 Hz), 49.2 (d, $^3J_{P-C}$ = 2.4 Hz), 24.0, 15.9 (d, $^3J_{P-C}$ = 6.2 Hz), 14.5 (s); $^{31}$P NMR $\delta$ 4.7; IR (neat) 1253 (s), 1116 (s), 1032 (s) cm$^{-1}$; MS (EI) 279 (M$^+$, 0.3), 126 (40), 98 (73), 80 (100), 78 (79); HRMS calcd for $C_{10}H_{18}NO_4SP$ 279.0690, found 279.0693.

***exo*-3-Aza-*N*-(diethoxylphosphoryl)-2-oxo-2-thiabicyclo[2.2.2]oct-5-ene (7a′, minor sulfur epimer).** Oil; 6%; $^1$H NMR $\delta$ 6.79−6.74 (m, 1H), 6.33−6.27 (m, 1H), 4.09−4.03 (m, 1H), 4.10−4.02 (m, 4H), 3.99−3.93 (m, 1H), 2.85−2.78 (m, 1H), 2.28−2.2 (m, 1H), 1.52−1.34 (m, 2H), 1.29−1.24 (m, 6H); $^{13}$C NMR $\delta$ 139.5 (d, $J$ = 4.9 Hz), 127.5, 62.7 (d, $J$ = 12.2 Hz), 62.4 (d, $J$ = 12.2 Hz), 54.8 (d), 48.3, 24.1, 15.0 (d), 10.5; $^{31}$P NMR $\delta$ 4.9; IR (neat) 1264 (s), 1114 (s), 1024 (s) cm$^{-1}$; MS (EI) 279 (M$^+$, 0.3), 126 (37), 98 (63), 80 (100), 79 (56).

***endo*-3-Aza-*N*-(dimethoxylphosphoryl)-2-oxo-2-thiabicyclo[2.2.2]oct-5-ene (7b, major sulfur epimer).** White crystals; 72%; eluting (2/5 hex/THF); mp 96−97.5 °C (EtOAc); $^1$H NMR $\delta$ 6.97−6.92 (m, 1H), 6.28 (t, $^2J_{H-H}$ = 7.4 Hz, 1H), 4.68−4.65 (m, 1H), 4.36−4.31 (m, 1H), 3.81 (d, $^2J_{P-H}$ = 12.9 Hz, 3H), 3.77 (d, $^2J_{P-H}$ = 12.9 Hz, 3H), 1.84−1.72 (m, 2H), 1.62−1.51 (m, 1H), 1.24−1.13 (m, 1H); $^{13}$C NMR $\delta$ 137.0 (d, $^3J_{C-P}$ = 4.9 Hz), 125.4, 55.5 (d, $^2J$ = 4.9 Hz), 54.3 (d, $^2J$ = 6.1 Hz), 53.9 (d, $^3J$ = 4.9 Hz), 49.8 (d, $^3J$ = 2.4 Hz), 24.4, 14.8; $^{31}$P NMR $\delta$ 7.6; IR (KBr) 1267 (s), 1106 (s), 1012 (s) cm$^{-1}$. Anal. Calcd for $C_8H_{14}NO_4SP$: C, 38.25; H, 5.62; N, 5.58. Found: C, 38.34; H, 5.66; N, 5.61.

***exo*-3-Aza-*N*-(dimethoxylphosphoryl)-2-oxo-2-thiabicyclo[2.2.2]oct-5-ene (7b′, minor sulfur epimer).** Oil; 6%; $^1$H NMR $\delta$ 6.77−6.72 (m, 1H), 6.29 (t, $J$ = 7.52 Hz, 1H), 4.39−4.35 (m, 1H), 3.95−3.90 (m, 1H), 3.77 (d, $J$ = 11.43 Hz, 3H), 3.75 (d, $J$ = 11.5 Hz, 3H), 2.83−2.75 (m, 1H), 2.26−2.18 (m, 1H), 1.62−1.40 (m, 2H); $^{13}$C NMR $\delta$ 140.8, 128.6, 56.0 (d, $J$ = 4.9 Hz), 55.1 (d, $J$ = 4.9 Hz), 53.7 (d, $J$ = 4.9 Hz), 49.5, 25.2 (d, $J$ = 4.9 Hz), 11.5; $^{31}$P NMR $\delta$ 7.8; IR (neat) 1233 (s), 1100 (s), 1032 (s) cm$^{-1}$.

**Method b: General Procedure for Adducts (7c, 4d−7d, 7e, 7f).** Freshly prepared N-(chlorosulfinyl)imidazole[8] (15 mmol) was added to a solution of phosphoramidate (15 mmol) and $CH_2Cl_2$ (10 mL) at −40 °C. The resulting mixture was stirred at room temperature for 2−6 h. After removal of the salt and solvent, the residue was dissolved in anhydrous $CH_2Cl_2$ (10 mL). A diene (20 mmol) was added to the $CH_2Cl_2$ solution, and then the mixture was stirred at room temperature for 5−10 h. Workup and purification was carried out as those for method a.

***endo*-3-Aza-*N*-(diphenylphosphoryl)-2-oxo-2-thiabicyclo[2.2.2]oct-5-ene (7c).** White powders; 50%; eluting (1.5% MeOH/$CHCl_3$); mp 134−135 °C (EtOAc); $^1$H NMR $\delta$ 8.02−7.95 (m, 4H), 7.85−7.78 (m, $J$ = 12.8 Hz, 3H), 7.62−7.41 (m, 3H), 6.89 (t, $J$ = 7.2 Hz, 1H), 6.31 (t, $J$ = 7.4 Hz, 1H), 4.62−4.56 (m, 1H), 4.28 (br, 1H), 2.14−2.08 (m, 1H), 1.75−1.61 (m, 2H), 1.25−1.11 (m, 1H); $^{13}$C NMR $\delta$ 137.3, 137.2, 133.3, 132.8, 132.6, 129.2, 128.6, 128.1, 126.3, 56.1 (d, $J$ = 3.7 Hz), 49.9 (d, $J$ = 4.9 Hz), 25.1, 15.2; $^{31}$P NMR $\delta$ 29.5; IR (KBr) 1212 (s), 1154, 1118 (s), 1053 (s) cm$^{-1}$. Anal. Calcd for $C_{18}H_{18}NO_2SP$: C, 62.94; H, 5.28; N, 4.08. Found: C, 63.14; H, 5.32; N, 4.18.

**2-(5,5-Dimethyl-2-oxo-1,3,2-dioxaphosphoryl)-3,6-dihydro-2*H*-1,2-thiazine 1-Oxide (4d).** Oil; 40%; eluting (1% MeOH/$CHCl_3$); $^1$H NMR $\delta$ 6.06−5.99 (m, 1H), 5.79−5.72 (m, 1H), 4.35−4.27 (m, 2H), 4.09−3.96 (m, 2H), 3.92−3.67 (m, 2H), 3.53−3.44 (m, 1H), 3.33−3.27 (m, 1H), 1.22 (s, 3H), 1.00 (s, 3H); $^{13}$C NMR $\delta$ 124.7 (d, $J$ = 6.1 Hz), 114.4, 77.5 (d, $J$ = 6.1 Hz), 76.7 (d, $J$ = 6.1 Hz), 48.3 (d, $J$ = 4.9 Hz), 37.0 (d, $J$ = 3.7 Hz), 31.9, 21.9, 20.8; $^{31}$P NMR $\delta$ −1.4; IR (neat) 1261 (s), 1160

(22) (a) Israili, Z. H.; Perel, J. M. *J. Med. Chem.* **1972**, *15*, 709. (b) Deyrup, J. A.; Moyer, C. L. *J. Org. Chem.* **1969**, *34*, 175.

(s), 1058, 1006 (s) $cm^{-1}$; MS (EI) 265 ($M^+$, 13), 212 (29), 144 (35), 69 (100); HRMS calcd for $C_9H_{16}NO_4SP$ 265.0534, found 265.0540.

**2-(5,5-Dimethyl-2-oxo-1,3,2-dioxaphosphoryl)-5-methyl-3,6-dihydro-2*H*-1,2-thiazine 1-Oxide (5d).** Oil; 52%; eluting (2% MeOH/$CHCl_3$); $^1H$ NMR $\delta$ 5.73 (br, 1H), 4.31−4.25 (m, 2H), 4.24−4.00 (m, 2H), 3.99−3.92 (m, 2H), 3.46 (bd, $J$ = 7.1 Hz, 1H), 3.13 (bd, 1H), 1.83 (br, 3H), 1.21 (s, 3H), 1.00 (s, 3H); $^{13}C$ NMR $\delta$ 132.1, 118.1 (d, $J$ = 6.1 Hz), 77.6 (d, $J$ = 6.1 Hz), 76.9 (d, $J$ = 6.1 Hz), 52.3 (d, $J$ = 4.9 Hz), 37.6 (d, $J$ = 3.7 Hz), 32.4 (d, $J$ = 6.1 Hz), 24.7 (d, $J$ = 1.2 Hz), 21.9, 21.0; $^{31}P$ NMR $\delta$ −1.4; IR (neat) 1283 (s), 1112 (s), 1013 (s) $cm^{-1}$; HRMS calcd for $C_{10}H_{18}NO_4SP$ 279.0694, found 279.0693.

**2-(5,5-Dimethyl-2-oxo-1,3,2-dioxaphosphoryl)-4,5-dimethyl-3,6-dihydro-2*H*-1,2-thiazine 1-Oxide (6d).** White powders; 65%; eluting (2% MeOH/$CHCl_3$); mp 128−131 °C; $^1H$ NMR $\delta$ 4.33−4.24 (m, 2H), 4.06−3.92 (m, 2H), 3.88 (br, 2H), 3.52 (bd, $J$ = 6.8 Hz, 1H), 3.11 (bd, $J$ = 6.4 Hz, 1H), 1.79 (s, 3H), 1.75 (s, 3H), 1.20 (s, 3H), 1.02 (s, 3H); $^{13}C$ NMR $\delta$ 131.8, 116.9, 77.7 (d, $J$ = 4.9 Hz), 76.8 (d, $J$ = 4.9 Hz), 53.7 (d, $J$ = 4.9 Hz), 41.5 (d, $J$ = 3.7 Hz), 31.8 (d, $J$ = 4.9 Hz), 21.8, 21.0, 19.8, 17.0; $^{31}P$ NMR $\delta$ −1.7; IR (KBr) 1258 (s), 1144 (s), 1094, 1054 (s) $cm^{-1}$. Anal. Calcd for $C_{11}H_{20}NO_4SP$: C, 43.11; H, 7.07; N, 4.95. Found: C, 43.24; H, 6.92; N, 4.81.

***endo*-3-Aza-3-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphoryl)-3-oxo-3-thiabicyclo[2.2.2]oct-5-ene (7d).** Oil; 45%; eluting (2/5 hex/THF); $^1H$ NMR $\delta$ 6.98−6.92 (m, 1H), 6.33−6.28 (m, 1H), 4.69−4.67 (br, 1H), 4.36−4.35 (br, 1H), 4.32−4.25 (m, 1H), 4.18−4.03 (m, 3H), 2.13−1.96 (m, 1H), 1.76−1.70 (m, 1H), 1.68−1.54 (m, 1H), 1.30−1.27 (m, 1H), 1.17 (s, 3H), 1.03 (s, 3H); $^{13}C$ NMR $\delta$ 136.5, 125.4, 77.6 (d, $J$ = 4.9 Hz), 76.8 (d, $J$ = 4.9 Hz), 54.2, 49.2, 24.5 (d, $J$ = 3.7 Hz), 21.6, 21.1, 15.6; $^{31}P$ NMR $\delta$ −1.0; IR (neat) 1227 (s), 1123 (m), 1060, 1011 (s) $cm^{-1}$; MS (EI) 291 ($M^+$), 191 (87), 166 (68), 123 (53), 98 (100), 79 (50). A byproduct **8d** was isolated in 20% yield.

***endo*-3-Aza-3-(3-*n*-propyl-1,3,2-oxazaphosphoryl)-2-oxo-2-thiabicyclo[2.2.2]oct-5-ene (7e).** Oil; 55% (two diastereomers); eluting (2/5 hex/THF); $^1H$ NMR $\delta$ 6.98−6.95 (m, 1H), 6.26 (t, $J$ = 7.3 Hz, 1H), 4.83−4.78 (m, 1H), 4.58−4.52 (m, minor isomer), 4.41−4.25 (m, 3H), 3.51−3.44 (m, minor), 3.32−3.30 (m, 1H), 3.18−3.03 (m, 2H), 2.95−2.78 (m, 1H), 2.06−1.97 (m, 2H), 1.90−1.72 (m, 2H), 1.69−1.56 (m, 3H), 1.20−1.12 (m, 1H), 0.94−0.86 (m, 3H, two isomers); $^{13}C$ NMR $\delta$ 134.6, 127.6 (d, $J$ = 4.9 Hz), 67.7 (d, $J$ = 4.9 Hz), 54.9, 49.1 (d, $J$ = 3.7 Hz), 44.5, 25.1 (d, $J$ = 4.9 Hz), 23.4 (d, $J$ = 3.7 Hz), 20.2, 19.3 (d, $J$ = 3.7 Hz), 13.2; $^{31}P$ NMR $\delta$ 6.4/6.8 (56:44); IR (neat) 1254, 1243 (s), 1168, 1152 (m), 1005 (s) $cm^{-1}$; MS (ISP) 327 ($M^+$ + Na, 58), 247 (36), 225 (86), 211 (33), 197 (100).

***endo*-3-Aza-3-(3-*tert*-butyl-1,3,2-oxazaphosphoryl)-2-oxo-2-thiabicyclo[2.2.2]oct-5-ene (7f).** Oil; 41% (two diastereomers); eluting (2/5 hex/THF); $^1H$ NMR $\delta$ 6.93−6.87 (m, 1H), 6.26 (t, $J$ = 7.2 Hz, 1H), 4.85−4.83 (m, minor), 4.61−4.54 (m, 1H), 4.25−4.20 (m, 1H), 4.18−4.11 (m, 1H), 3.91−3.86 (m, 1H), 3.40−3.14 (m, 2H), 2.02−1.85 (m, 2H), 1.84−1.70 (m, 2H), 1.54−1.43 (m, minor), 1.35 (s, 9H), 1.31 (s, 1H), 1.15−1.01 (m, 1H); $^{13}C$ NMR $\delta$ 136.7 (d, $J$ = 4.9 Hz), 124.5, 56.0 (d, $J$ = 6.1 Hz), 49.9 (d, $J$ = 2.4 Hz), 26.1 (d, $J$ = 7.3 Hz), 14.5; $^{31}P$ NMR $\delta$ 4.1/4.8 (1:2); IR (neat) 1244 (s), 1155, 1104 (m), 1023 (s) $cm^{-1}$; MS (ESI) 319 ($M^+$ + 1, 19), 256 (100), 239 (100), 223 (64), 193 (79), 137 (79), 112 (14).

***N*-(Cyclohexa-3-enylamino)-5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinane (8d).** A $NaHCO_3$ 0.1 M solution (10 mL, 1 mmol) was added dropwise at room temperature to a solution of thiazine derivative (**7d**, 0.5 mmol) and $CH_2Cl_2$ (5 mL). The resulting solution was stirred for 30 min, cooled to 0 °C, and quenched by pouring into a mixture of 0.1 M HCl and ether. The aqueous portion was extracted with ether, and the combined organic extracts were washed with brine. The solution was dried ($MgSO_4$) and concentrated to give crude product. Flash chromatography of the crude (silica gel, 5% MeOH/$CHCl_3$) gave 0.1 g (61%) of **8d** as a white solid. Recrystallization from EtOAc: white crystals, mp 129−131 °C; $^1H$ NMR $\delta$ 5.68−5.55 (m, 2H), 4.33−4.28 (m, 2H), 3.85−3.74 (m, 2H), 3.48−3.41 (m, 1H), 2.89−2.82 (m, 1H), 2.41 (bd, $J$ = 7.9 Hz, 1H), 2.15−2.13 (m, 1H), 1.99−1.89 (m, 2H), 1.67−1.54 (m, 2H), 1.21 (s, 3H), 0.88 (s, 3H); $^{13}C$ NMR $\delta$ 125.1, 123.6, 74.4 (d, $J$ = 4.9 Hz), 46.1, 32.6 (d, $J$ = 6.1 Hz), 30.2, 29.4, 23.2, 19.6, 18.8; $^{31}P$ NMR $\delta$ 5.2; IR (KBr) 1229 (s), 1057, 1014 (s) $cm^{-1}$. Anal. Calcd for $C_{11}H_{20}NO_3P$: C, 53.87; H, 8.22; N, 5.71. Found: C, 53.82; H, 8.13; N, 5.71. The product was identical with the byproduct from the cycloaddition reaction of **3d**.

**Lewis Acid-Catalyzed Cycloaddition Reactions. General procedure.** To a solution of *N*-sulfinylphosphoramidate (2.0 mmol, freshly prepared in situ from the phosphoramidates) in $CH_2Cl_2$ (5 mL) was added $SnCl_4$ (1.8 mmol) at −78 °C. After the mixture was stirred for 5 min, cyclohexadiene (4 mmol) was added, and the resultant mixture was stirred for 10−20 min at −78 °C. The mixture was poured into water (10 mL) and extracted with $CH_2Cl_2$ (3 × 15 mL). The combined organics were washed with brine and dried over $Na_2SO_4$. The same procedure was used for the separation and purification as that for the thermal cycloaddition reactions. See Table 2 (reaction conditions and isolated yields). In all case, the acid-catalyzed reactions provided only one isomer, and the purity was checked by $^{31}P$ and $^1H$ NMR.

**Tin chelate 15.** $SnCl_4$ (0.29 g, 1 equiv) was added to the diethyl *N*-sulfinylphosphoramidate freshly distilled (**3a**, 0.2 g, 1.15 mmol) and $CH_2Cl_2$ (6 mL) at −78 °C under nitrogen. To this stirred mixture was added dropwise a precooled (−30 °C) solution of an excess (0.18 g, 2.5 equiv) of cyclohexadiene in $CH_2Cl_2$ (1 mL). The reaction mixture was stirred at −78 °C for 30 min. The white precipitate was collected by filtration. The mother liquor yielded more product after cooling the solution. Recrystallization from EtOAc gave 0.41 g (72%). White powder; mp 112−114 °C; $^1H$ NMR ($CD_3COCD_3$) $\delta$ 7.06−7.00 (m, 1H), 6.37−6.32 (m, 1H), 4.82 (br, 1H), 4.68 (br, 1H), 4.38−4.25 (m, 4H), 1.90−1.81 (m, 2H), 1.76−1.65 (m, 1H), 1.41−1.35 (m, 6H), 1.28−1.25 (m, 1H); $^{13}C$ NMR (DMSO-$d_6$) $\delta$ 136.4 (d, $J$ = 3.7 Hz), 125.7, 62.6 (d, $J$ = 12.2 Hz), 62.4 (d, $J$ = 12.2 Hz), 54.6 (d, $J$ = 4.9 Hz), 48.9, 23.8, 15.8 (d, $J$ = 6.1 Hz), 14.3; $^{31}P$ NMR (DMSO-$d_6$) $\delta$ 4.4; IR (KBr) 1203 (s), 1161 (m), 1028 (s) $cm^{-1}$; $^{119}Sn$ NMR (external $SnCl_4$) $\delta$ −952. Anal. Calcd for $C_{10}H_{18}Cl_4NO_4SPSn$: C, 22.23, H, 3.37 N, 2.60; Cl, 25.96. Found: C, 21.82; H, 3.69; N, 2.43; Cl, 26.32.

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**Supporting Information Available:** $^1H$ NMR spectra for **4d**, **6a**, **7a**, **7a′**, **7b**, **7b′**, **7d**, **7e**, **7f**, **9d** and $^{13}C$ NMR for **3d**, **5a**, **5d** (13 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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