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(*R*)-4-phenyloxazolidin-2-thione: an efficient chiral auxiliary for [4+2] cycloaddition of 1-aminodiene and activated phosphonodienophiles

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ABSTRACT

A theoretical model for the facial selectivity of *N*-dienyl oxazolidin-2-(thi)one and thiazolidin-2-thione **2a–c** is presented. Our analysis provides a clear understanding of factors controlling stereoselectivity in reaction of these dienes, and allows predictions of high diastereoselectivity in the case of oxazolidin-2-thionyl diene (**2b**). The application of this diene to the synthesis of β- and γ-aminophosphonic derivatives is then investigated. Under classical conditions or under microwave activation, the D–A reaction of diene **2b** leads to aminophosphonic chirons with high regio- and stereoselectivities.

The Diels–Alder (D–A) reaction occupies a central role in organic synthesis as it generates polyfunctionalized six-membered rings with high regio- and stereo-control.[1] Numerous examples of asymmetric D–A reactions (chiral auxiliaries,[2] chiral catalysts,[3] organocatalysts,[4] chiral media,[5] etc.) have also shown that it is possible to control the absolute configuration of cycloadducts. In this context, we recently reported[8b–e] the successful development of a new chiral N-protected aminodiene[8f–k] based on a simplified theoretical model (model compounds **1a–b**, R^1 = H; see Fig. 1) and its use in asymmetric D–A reactions.

The compatibility of the D–A reaction with a wide range of chemical functions guarantees interest in many research areas, from simple molecules to large and complex structures. Also, the implementation of modern synthesis techniques[6,7] (microwave activation, high pressure reactors, micro-emulsions, etc.) overcomes previous unsuccessful applications of the D–A process due to low reactivity of the diene or/and the dienophile and instability of both partners and/or cycloadducts under thermal or Lewis acid-catalyzed conditions. This prompted us to envisage the use of diene **2** for the development of a general method for the asymmetric synthesis of aminophosphonic derivatives.[8a–e] These compounds are recognized as constituting an important class of pharmacologically active molecules.[9] Several strategies have been developed towards the α-amino phosphonic compounds, related to the naturally occurring α-aminoacids.[10] Surprisingly, β-, γ- and δ-aminophosphonic derivatives were obtained only via punctual methods.[9a,11]

In this Letter, we document further the theoretical model[12,13] for the facial selectivity of dienes bearing thiazolidin-2-(thi)one

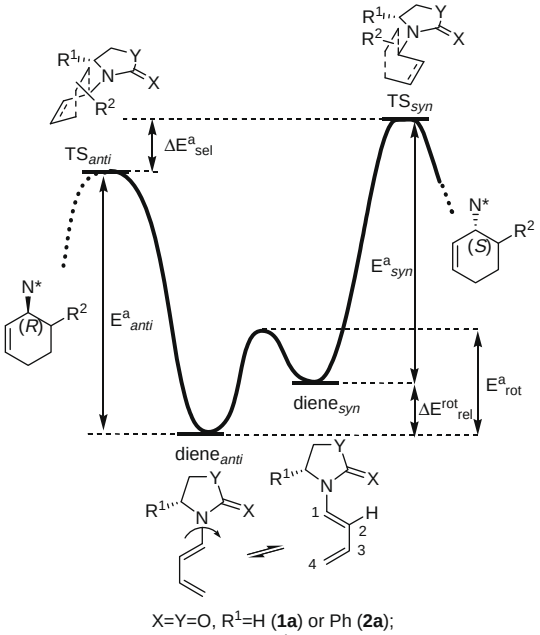

Figure 1. Energy profiles for the cycloadditions of dienes **2a–c** (R^1 = Ph) and ethylene (R^2 = H) or propene (R^2 = Me).

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Table 1
Energetic discrimination between the two *anti* and *syn* conformers (ΔE^{rot}_{rel}) of dienes **2a–c** and selectivities (ΔE^{a}_{sel}) calculated for the D–A reaction between 2a-c (R^1 = Ph) and ethylene (R^2 = H) or propene (R^2 = Me) (values in brackets correspond to calculations in solution)

Diene	**2a** (X = Y = O)		**2b** (X = S, Y = O)		**2c** (X = Y = S)	
ΔE^{rot}_{rel} (kcal.mol^{-1})	*anti*	*syn*	*anti*	*syn*	*anti*	*syn*
	0	1.5 (1.7)	0	3.6 (3.7)	0	4.6 (4.4)
ΔE^{a}_{sel} (kcal.mol^{-1})	Ethylene	Propene[a]	Ethylene	Propene[a]	Ethylene	Propene[a]
	1.6 (1.8)	1.7 (1.1)	3.5 (3.1)	4.5 (3.9)	4.8 (4.5)	5.9 (5.2)

[a] Illustrated for the endo ortho cycloadducts.

or oxazolidin-2-thione chiral auxiliaries, using realistic systems and including now solvent effects. The application of aminodienes **2** for the asymmetric synthesis of β- and γ-aminophosphonic derivatives is then investigated.

The factors controlling the facial selectivity for chiral *N*-dienyl oxazolidin-2-(thi)ones **2a–b** and *N*-dienyl thiazolidin-2-thione **2c** (R^1 = Ph, Fig. 1) have been identified: the absolute configuration of the cycloadducts can be accounted for by the approach of the dienophile from the less hindered face (α-face)[14] of the *s-cis* diene presenting an *anti* conformation around the C(1)–N bond (see Fig. 1).[8c–e] Indeed, this conformation was found to be preferred over the *syn* one because of (1) the higher stabilization by electronic delocalization involved in the *anti* orientation, (2) the unfavourable orientation of respective dipoles of the dienyl and heterocyclic moieties in the *syn* conformer and despite (3) the emergence of a stabilizing electrostatic interaction between oxygen and the nearest hydrogen in the *syn* isomer (Table 1).

Our calculations[12a] on realistic models and taking solvents effects into account predict that structural modification by successive oxygen–sulfur replacement (compounds **2a–c**) leads to an increase of the energetic discrimination between the *syn* and the *anti* conformers by further (relative) destabilization of the former (Table 1). The most important effect is observed when going from oxazolidin-2-one **2a** to oxazolidin-2-thione **2b**, most probably due to a weaker stabilizing effect by the hydrogen bond in the *syn* conformer.[8e,15] Indeed, similar trends observed in solution phase suggest that the dipole–dipole interaction between butadienyl and heterocyclic moieties is not a determining factor for the *anti–syn* energetic discrimination. Also, the fact that the rotation barrier was found to be constant[16] (ΔE^{a}_{rot} is about 9.5 kcal mol^{-1} for dienes 2a–**c**) indicates that oxygen–sulfur replacement does not affect significantly electronic delocalization.

Our calculations on TSs confirm the increase of facial selectivity upon progressive replacement of oxygen by sulfur (Table 1). The main effect is observed for the oxazolidin-2-one (**2a**) to oxazolidin-2-thione (**2b**) shift. A structural analysis of the TSs shows a systematic concerted synchronous addition (Fig. 2). Activation barriers for both regioisomers (*ortho* and *meta*) for propene cyclization indicated a slight preference for the *ortho*-pathway (by 0.5 kcal mol^{-1}) with no particular effect comparing the three dienes **2a–c**. This low regioselectivity arises from the low activating effect of the methyl group of propene, and should be stronger when considering more activated dienophiles. Generally, the results collected indicate that the *endo* approach is favoured over the *exo*. Interestingly, the cycloaddition of the sulfur-containing dienes (compounds **2b–c**) with

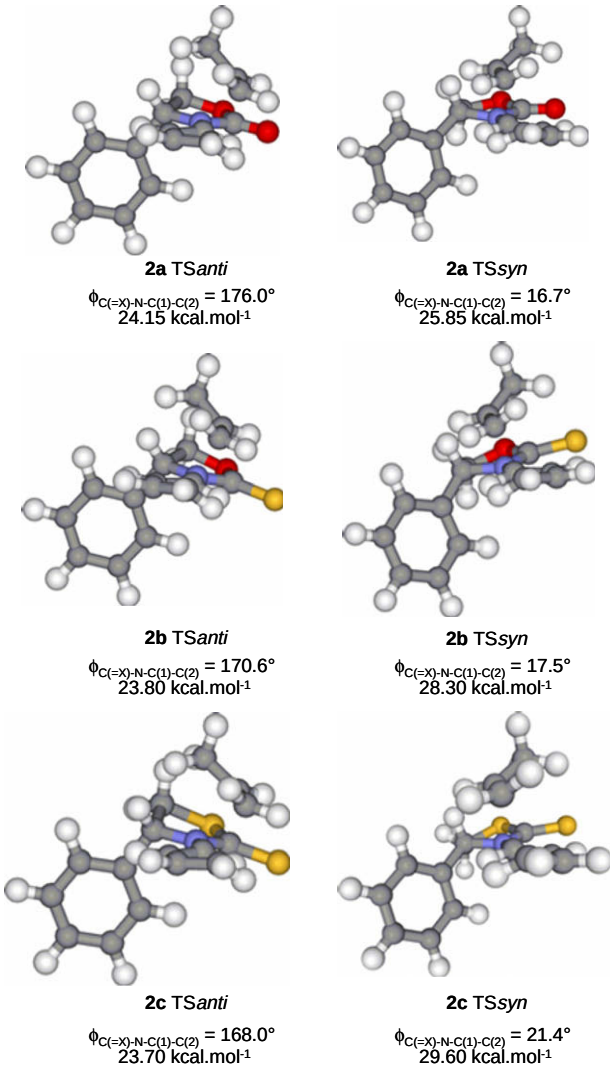
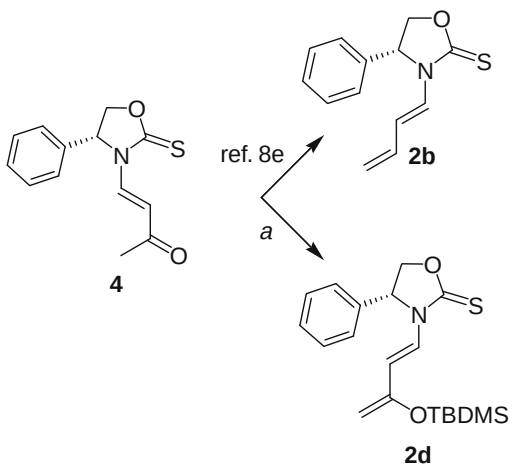
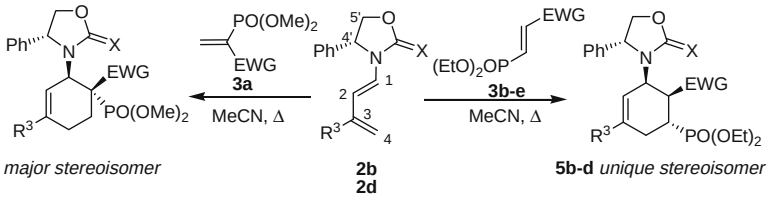


Figure 2. Structure and energy of two relevant transition states for the cycloaddition of propene and dienes **2a–c** (Energy of both transition states is relative to the sum of the reactants energies considering the diene in its *anti* conformation).

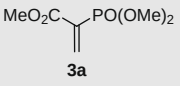
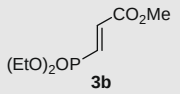
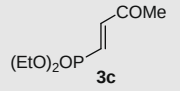
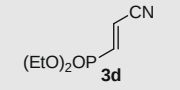
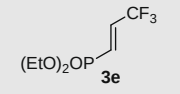


Scheme 1. Synthesis of dienes **2b** and **2d**. Reagent ands conditions: (a) TBDMSCl, NaI, Et_3N, rt, overnight (**2b**, quant.).



Scheme 2. Cycloaddition of dienes **2b** and **2d** with the selected dienophiles **3a–e**.

Table 2
Cycloadditions of dienes **2b** with the selected dienophiles (**3a–e**)

Entry	Dienophile	X	Yield[a]	Regioselect.[b]	*endo/exo*	de[c]
1	 **3a**	O	80	100	84:16	80
2		S	>98	100	**86:14**	**>99**
3	 **3b**	O	69	100	76:24	82
4		S	73	100	**100:0**	**>99**
5	 **3c**	O	63	100	92:8	95
6		S	70	100	**100:0**	**>99**
7	 **3d**	O	59	100	85:15	>85
8		S	54	100	**100:0**	**>99**
9	 **3e**	O	0	/	/	/
10		S	0	/	/	/

[a] After purification by column chromatography.
[b] Determined by ^{1}H NMR (500 MHz) analysis on the crude mixtures.
[c] (3*R*) isomer versus (3*S*) isomer, for the major *endo*-stereoisomer.

propene is characterized by a higher *endo/exo* selectivity as compared to the oxazolidin-2-one diene **2a**.

Since the most important effects were predicted for diene **2b**, we selected the latter for the development of an asymmetric synthesis of β- and γ-aminophosphonates. Our strategy is based on the fact that the regioselectivity of the D–A reaction should allow the selective synthesis of β- and γ-aminophosphonic derivatives by reaction of diene **2b** with unsymmetrical *gem*- and *vic*-activated phosphonodienes, respectively.[17] Diene **2b** was synthesized from intermediate **4** according to the reported procedure (Scheme 1).[8e] The corresponding 3-siloxy-activated diene **2d**[18] was also obtained quantitatively from the vinylogous amide **4**, in view to enlarge the application field of the 4-phenyloxazolidin-2-thione chiral auxiliary.

Dienes **2b** and **2d** were engaged under classical conditions (refluxing MeCN) with the selected dienophiles (Scheme 2 and Table 2).

Degradation of the diene **2d** was observed in all cases, whereas diene **2b** reacts with phosphonodienophiles **3a–e** to give the corresponding amino-phosphonic derivatives with good yields. Low reactivity of phosphonodienophiles **3a–e** is, however, responsible for long reaction times (1–15 days). Nevertheless, the regioselectivity[19] and the reactivity order are compatible with the orientation and the strength of the polarization among the π system of the dienophiles **3a–e**. Surprisingly, dienophile **3e** remains unreactive even under prolonged heating. Thermal instability of the cycloadducts prevented, in most cases, the use of GC for the determination of selectivities, but 500 MHz NMR analysis of the crude mixtures offered a convenient tool for structural assignments.[19] In each case, the facial discrimination induced by the chiral 4-phenyloxazolidin-2-thione auxiliary is total. Endo-selectivity is also total for dienophiles **3b–d**; in the case of the *gem*-substituted phosphonodienophile **3a**, endo-selectivity drops to 86/14 (Table 2, entry 1), mainly because of steric hindrance. What is very encouraging is the observed enhancement of the facial selectivity as compared to the oxazolidin-2-one series (X = O).[8e–k] This structural modification does not affect the intrinsic reactivity of the diene as indicated by similar yields and reaction times.

Table 3
Microwave activation assays illustrated for the reaction of **2b** and **3c**

Solvent	Power (W)	Temp. (°C)	Time (h)	Conv. (%)
Toluene	300	60	24	0
$(CH_2Cl)_2$	500	75	24	15
MeCN	750	80	24	22
DMF	500	145	4	100

Despite the excellent regio- and stereoselectivities offered by the chiral aminodiene **2b**, the application field suffers from the lack of reactivity of the phosphonodienophiles. Microwave (MW) activation could provide a useful way to overcome this inherent low reactivity. Using toluene or dichloromethane as solvent (totally permeable to MW), no, or very low, conversion was observed after prolonged heating (Table 3). However, in acetonitrile, conversion occurred to the same extent as under classical heating conditions and in DMF, at 145 °C, complete conversion was observed after only 4 h. These observations highlight the lack of specific MW activation effect as a consequence of an isopolar mechanism[20] (in good agreement with the predicted concerted synchronous character of these cycloadditions, see above). There is no modification of the observed selectivities under microwave activation. Dienophile **3e** remains unreactive towards diene **2b**, and no D–A reaction of diene **2d** was observed. This MW activation method allows an increased efficiency to reach the corresponding cycloadducts **5a–d**. Complete structural analysis of these cycloadducts has been published elsewhere.[8b,d]

In summary, we have further illustrated the D–A cycloadditions of chiral *N*-oxazolidin-2-thione diene **2b** with a representative set of *gem*- and *vic*- activated phosphonodienophiles (**3a–d**). Under both thermal conditions and MW activation, these reactions proceed with total regio- and stereoselectivities, leading to β- and γ-aminophosphonic chirons.[21] Our computational investigation, on realistic model and including solvent effects, of the factors governing the stereoselectivity provides a complete rational for the asymmetric D–A reaction of N-protected dienes bearing a oxazolidin-2-(thi)one or thiazolidin-2-thione moiety. This study shows that fa-

cial selectivity is controlled by the energetic discrimination between the two reactive conformers of the diene (*anti* and *syn* conformers). This energetic preference for the *anti* conformer increases with progressive oxygen–sulfur replacement in the chiral auxiliary. Calculations taking solvent effects into account indicate that the main factor responsible for the observed increase in facial selectivity upon going from oxazolidin-2-one to oxazolidin-2-thione chiral auxiliary is the lower stabilization of the *syn* conformer by hydrogen bond in the case of sulfur atom.

Acknowledgements

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13. Unconstrained optimizations were performed at the modified B3LYP/6-31G level (with supplementary *d* orbitals for sulfur atoms). SP energies were calculated at the B3LYP/6-31G** level.
14. The approach of the dienophile from the β-face of the diene was found to be disfavoured by about 5 kcal mol^{-1} (B3LYP/6-31G).
15. Due to the intrinsic geometrical features of the oxazolidin-2-one, oxazolidin-2-thione and thiazolidin-2-thione, we have observed an increased X···H–C(2) distance for compounds **2a–c** (2.28–2.61 Å).
16. ΔE^{a}_{rot} was found constant as a consequence of the conformational adaptability of the nitrogen atom.
17. Dienophile **3a** was commercially available. Dienophiles **3b–e** were synthesized from the described protocol in the literature. (a) McClure, C.; Hansen, K. *Tetrahedron Lett.* **1996**, *37*, 2149–2152; (b) Afarinkia, K.; Evans, M.; Graham, J.; Jimenez-Bueno, G. *Tetrahedron Lett.* **1998**, *39*, 433–434; (c) Nickson, T. *J. Org. Chem.* **1988**, *53*, 3870–3872.
18. A solution of (*R*)-3-(3′-oxobut-1′-enyl)-4-phenyloxazolidin-2-thione **4** (2.54 mmol, 0.63 g), TBDMSCl (3.2 mmol, 0.48 g) and triethylamine (3.2 mmol, 0.44 cm^3) in anhydrous MeCN (5 mL) was treated dropwise with an anhydrous solution of NaI (3.2 mmol, 0.48 g) in MeCN (2 mL) at room temperature over 10 min. After 15 h, the solution was concentrated under reduced pressure. The oily residue is diluted in petroleum ether (5 cm^3) and filtrated over a slight celite pad. Petroleum ether was removed under reduced pressure (temperature bath less 30 °C) to give pure **2d** as a yellow oil (0.91 g, >99%); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.67 (d, $J_{1,2}$ = 14.4 Hz, C(1)–H, 1H), 7.2–7.38 (m, 5H), 5.31 (d, $J_{2,1}$ = 14.4 Hz, C(2)–H, 1H), 5.21 (dd, $J_{4',5a'}$ = 9.0 Hz and $J_{4',5b'}$ = 4.4 Hz, C(4′)–H, 1H), 4.86 (t, $J_{5a',5b'}$ = 9.0 Hz, C(5′)–Ha, 1H), 4.36 (dd, $J_{5b',5a'}$ = 9.0 Hz, C(5′)–Hb 1H), 4.18 (s, C(4a)–H, 1H), 4.04 (s, C(4b)–H, 1H), 0.98 (s, 9H), 0.16 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 186.18 (s, C=S), 153.20 (s, C(3)), 137.23 (s, Cq φ), 129.46 (2 s, φ), 129.01 (s, φ), 126.01 (s, C(1)), 125.62 (s, φ), 114.29 (s, C(4)), 95.10 (s, C(2)), 74.81 (s, C(5′)), 62.04 (s, C(4′)), 25.70 (s, *t*-Bu), 18.06 (s, Cq *t*-Bu), -4.73 (s, Me), −4.87 (s, Me); IR (NaCl, ν, cm^{-1}): 2955, 1689, 1957, 1472, 1377, 1259, 1175; ESI MS m/z for $C_{19}H_{27}NO_2SSi$ [M+H$^+$]: 362.25 (18), 746.16 (100).
19. For a detailed structural analysis (by NMR and X-ray diffraction) of cycloadducts **5a–d**, see Refs. 8b and 8d.
20. (a) Loupy, A.; Maurel, F.; Sabatie-Gogova, A. *Tetrahedron* **2004**, *60*, 1683–1691; (b) Diaz-Ortiz, A.; Carrillo, J.; Cossio, F.; Gomez-Escalonilla, M.; de la Hoz, A.; Moreno, A.; Prieto, P. *Tetrahedron* **2000**, *56*, 1569–1577; (c) Langa, F.; de la Cruz, P.; de la Hoz, A.; Espildora, E.; Cossio, F.; Lecea, B. *J. Org. Chem.* **2000**, *65*, 2499–2507.
21. We have shown in a previous paper (see Monbaliu, J.-C.; Tinant, B.; Marchand-Brynaert, J. *Heterocycles* **2008**, *75*, 2459–2475) that oxazolidin-2-thione could be (quantitatively) transformed into their oxazolidin-2-one analogues for which several deprotection methods (to lead to corresponding primary amine) have been reported. See: (a) Turconi, J.; Lebeau, L.; Paris, J.-M.; Mioskowski, C. *Tetrahedron* **2006**, *62*, 8109–8114; (b) Fisher, J.; Duningan, J.; Hatfield, L.; Hoying, R.; Ray, J.; Thomas, K. *Tetrahedron Lett.* **1993**, *34*, 4755–4758; (c) Katz, S.; Bergmeier, S. *Tetrahedron Lett.* **2002**, *43*, 557–559.