[6] $HPCy_2$ and $HP(tBu)_2$ were obtained from Strem Chem. Co.; $HPNor_2$, **6**, and **7** were obtained from Cytec Chem. Co.; $HPAd_2$ was synthesized according to J. R. Goerlich, R. Schmutzler, *Phosphorus Sulfur Silicon Relat. Elem.* **1995**, *102*, 211.

[7] Synthetic procedures: General: Usually, only GLC yields were determined (internal standard). Where investigated, the yields of the isolated products were in a comparable range.[4] *Suzuki reaction*: Phenylboronic acid (1.5 mmol), 4-chloroanisole (1 mmol), and K_3PO_4 (3 mmol) in dioxane (2 mL) were heated to 100 °C. A solution of the catalyst was prepared by mixing the palladacycle (0.01 mmol Pd) with a solution of the ligand (0.015 mmol) in dioxane (0.2 mL), and it was added to the hot reaction mixture. The reaction mixture was stirred for 20 h. Samples were withdrawn by syringe and analyzed by GLC. *Heck reaction*: Sodium carbonate (7.5 mmol) was placed in a Schlenk tube under argon. Degassed *N*,*N*-dimethylacetamide (DMAc, 4 mL), 4-chlorotoluene (5 mmol), butyl acrylate (7.5 mmol), and diethylene glycol dibutyl ether (internal standard) were added, and the reaction mixture was heated to 140 °C. A solution of the catalyst **1** (0.1 mmol) in DMAc (1 mL) was added by syringe to the hot reaction mixture. The reaction mixture was stirred for 20 h. After cooling the reaction mixture to room temperature, it was partitioned between diethyl ether and water, and the organic phase was analyzed by GLC. *Arylation reaction*: NaO*t*Bu (3.9 mmol) was placed in a Schlenk tube under argon. Degassed toluene (3 mL), 4-chlorotoluene (3 mmol), and propiophenone (3.6 mmol) were added, and the reaction mixture was stirred for 30 minutes at room temperature. It was then heated to 110 °C, and a solution of the catalyst **1** (0.06 mmol) in toluene (1 mL) was added by syringe to the hot reaction mixture. The reaction mixture was stirred for 15 h. After cooling the reaction mixture to room temperature, it was partitioned between *tert*-butyl methyl ether (TBME) and water, and the organic phase was analyzed by GLC. *Amination reactions*: NaO*t*Bu (4.2 mmol) was placed in a Schlenk tube under argon. Degassed toluene (3 mL), aryl chloride (3 mmol), and amine (3.6 mmol) were added, and the reaction mixture was stirred for 30 min at room temperature. It was then heated to 110 °C, and a solution of the catalyst **1** (0.06 mmol) in toluene (1 mL) was added by syringe to the hot reaction mixture. The reaction mixture was stirred for 15 h. After cooling the reaction mixture to room temperature, it was partitioned between TBME and water, and the organic phase was analyzed by GLC.

[8] A. F. Littke, G. C. Fu, *Angew. Chem.* **1998**, *110*, 3586; *Angew. Chem. Int. Ed.* **1998**, *37*, 3387; A. F. Littke, G. C. Fu, *J. Org. Chem.* **1999**, *64*, 10.

[9] General procedure: Complexes **9**–**12** were easily prepared by adding the appropriate phosphane to a degassed suspension of the dimeric palladacyclic chloride **8** in dichloromethane under argon. The resulting complexes are soluble and the solutions are stable against hydrolysis and oxidation by air. Some metallic palladium was removed by filtering the solution through a plug of silica. The solutions were concentrated to a minimal volume and the complexes precipitated with hexane. Complexes **9**–**12** were obtained as yellow to brownish yellow powders in medium to high yields that were completely odorless and air stable for at least several months. (For details see the Supporting Information).

[10] Unfortunately, the complex with the best ligand, $P(tBu)_3$[7], was not stable and could not be isolated.

[11] R. B. Bedford, C. S. J. Cazin, *Chem. Commun.* **2001**, 1540.

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[14] a) D. W. Old, J. P. Wolfe, S. L. Buchwald, *J. Am. Chem. Soc.* **1998**, *120*, 9722; b) J. M. Fox, X. Huang, A. Chieffi, S. L. Buchwald, *J. Am. Chem. Soc.* **2000**, *122*, 1360.

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[16] A. Indolese, Solvias, unpublished results.

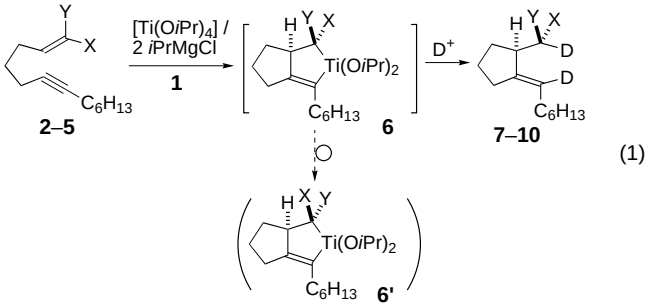
[17] This complex is commercially available in laboratory quantities from Strem and in technical quantities from Solvias AG.

Sulfur-Functionalized Olefins for Titanacycle Formation: Tandem Asymmetric Cyclization and the Pummerer Reaction Based on Sulfoxides Promoted by Titanium(II)-to-Titanium(IV) Relay**

Miho Narita, Hirokazu Urabe, and Fumie Sato*

Sulfur functional groups such as sulfides, sulfoxides, and sulfones have found numerous and pivotal applications in organic synthesis.[1] When enynes having a sulfur functional group are subjected to cyclization mediated by (stoichiometric) group-four transition metals,[2,3] the formation of new sulfur-functionalized metallacycles is expected and their behavior should be of considerable interest. Considering that study along this line is so far notably limited,[4] we report here new aspects of the use of vinylic sulfur functional groups in the titanium alkoxide-mediated enyne cyclization.

First, the viability of the cyclization of enynes having a vinylic sulfide, sulfone, or sulfoxide moiety with a Ti^{II} alkoxide reagent, $[Ti(OiPr)_4]/2\,i$PrMgCl (**1**),[3] was briefly surveyed [Eq. (1)].



(1)

The *E*- and *Z*-vinyl sulfides **2** and **3** underwent clean and, more importantly, stereospecific and stereoselective cyclization to the most likely titanacycles **6**, which underwent deuteriolysis to give the isomeric deuterated products **7** and **8**, respectively [Eq. (1) and entries 1 and 2, Table 1].[5,6] Analogously, the *E*-vinyl sulfone **4** afforded **9** (entry 3) upon deuteriolysis, which suggests the selective generation of the titanacycle **6**. Contrarily, the *Z*-vinyl sulfone **5** gave a mixture of **10** (minor constituent) and **9** (as a major component; entry 4), which indicates that the stereochemical integrity of **5**

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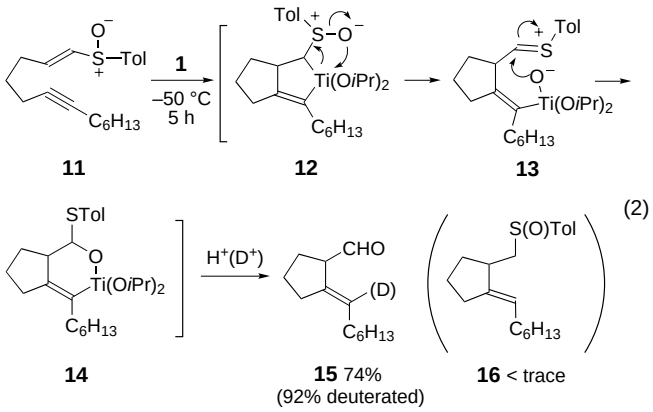
Table 1. Stereospecificity in the cyclization of sulfides and sulfones according to Eq. (1).[a]

Entry	Enyne X	Y		*E*/*Z*		Product Yield [%][b]	D [%][c,d]	Isomers	Ratio[d]
1	SMe	H	**2**	pure *E*	**7**	73	97	**7**/**8**	>99:<1
2	H	SMe	**3**	8:92	**8**	76	99	**8**/**7**	93:7 (100:0[e])
3	SO_2Ph	H	**4**	pure *E*	**9**	98	94	**9**/**10**	94:6
4	H	SO_2Ph	**5**	2:98	**10**	79	98	**10**/**9**	23:77

[a] The reaction temperatures were −50 °C for sulfides and −20 °C for sulfones; these were essential to complete the cyclization. [b] Combined yield of isomers. [c] Total deuterium incorporation at the carbon atom α to X and Y. (The olefinic position was also deuterated to a high degree.) [d] Determined by ^{1}H NMR spectroscopic analysis. [e] Corrected to pure *Z*-vinyl sulfide.

was lost, probably caused by the isomerization of **6** to the less sterically congested **6′** under these reaction conditions.[7] Stereodefined titanacyclopentenes such as those generated as shown in entries 1–3 of Table 1 should find use for the stereoselective construction of cyclic systems.[7]

In contrast to the two above-mentioned sulfur compounds, the corresponding sulfoxide **11** did not afford the expected cyclization product **16** but, instead, the cyclic aldehyde **15** [Eq. (2); Tol = *p*-tolyl].

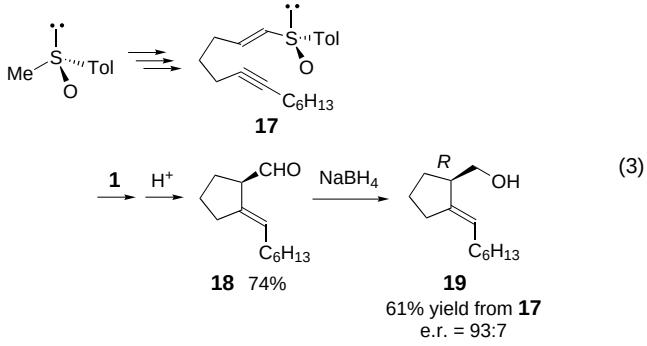


(2)

The formation of **15** could be rationalized by the **1**-mediated cyclization of **11** giving the titanacycle **12**, followed by the subsequent Pummerer-type rearrangement (**12**→**13**→**14**)[8] to furnish the aldehyde **15** after aqueous workup. In fact, the presence of the remaining carbon–titanium bond in **14** was confirmed by deuteriolysis experiments and may be used for further synthetic elaboration.[9] Surprisingly, this Pummerer reaction proceeded at a very low temperature compared to other standard procedures.[8] The presence of an anionic moiety α to the sulfoxide, and the Lewis acidity of the proximate titanium(IV) center,[10] may account for this extremely facile rearrangement even at a low temperature.

We then proceeded to the next stage, an asymmetric cyclization, taking advantage of a chiral sulfoxide moiety.[11] Equation (3) illustrates this transformation, showing a high chirality induction at the cyclization step.[12]

The enantiomeric ratio (e.r.), as well as the absolute configuration of aldehyde **18**, was unambiguously determined by derivatization to **19** and further correlation to a known compound. Additional results are summarized in Table 2. The stereochemistry of the exocyclic, trisubstituted double bond of the produced aldehydes was established as *E* by an NOE study in a representative case. When the terminal substituent



(3)

of acetylenes is more sterically demanding (**20** and **21**→**17**→**22**), the enantiomeric ratio of the products is slightly lowered (**24** and **25**→**18**→**26**). In contrast to the *E*-vinyl sulfoxides (entries 1–4), the less readily available *Z*-vinyl sulfoxide (**23**, entry 5) has no advantageous feature with respect to the chemical yield or enantiomeric ratio (with reversal of the absolute configuration as predicted from the following considerations). Scheme 1 shows a proposed mechanism for the production of *R*-aldehydes from *E*,*R*-vinyl sulfides. The sulfoxide oxygen atom coordinates to the titanium center to fix the structure as depicted, and the titanium–acetylene moiety approaches the carbon–carbon double bond on a reaction path that minimizes the steric repulsion (that is, the favored path, above in Scheme 1) to show the high degree of observed asymmetric induction.

In summary, by taking advantage of sulfur functional groups, we disclose herein the generation of new functionalized titanacycles and their subsequent reaction. Functional-group manipulation on a metal template, as illustrated by the Pummerer reaction on the titanacycle, may lead to new utility of metallacycles in organic synthesis.

Experimental Section

Typical procedure for **18**: To a stirred solution of **17** (100 mg, 0.316 mmol) and [Ti(O*i*Pr)$_4$] (0.117 mL, 0.395 mmol) in 5 mL of Et_2O was added *i*PrMgCl (1.34 M in Et_2O, 0.590 mL, 0.790 mmol) at −78 °C under argon. After stirring for 30 min, the solution was allowed to warm to −50 °C over 30 min and kept at this temperature for 5 h. Then, the reaction was quenched by the addition of aqueous 1N HCl at −50 °C. The organic layer was separated and washed with aqueous $NaHCO_3$ solution, dried over Na_2SO_4, and concentrated to leave an oil, ^{1}H NMR spectroscopic analysis of which revealed the crude yield of **18** to be 74%. The crude product was chromatographed on silica gel to afford **18** (43 mg, 70%) which was slightly contaminated by an unknown impurity (ca 10%). Further purification on TLC plates (Merck article no. 1.05554, 1% EtOAc in hexanes) afforded **18** (26.5 mg, 43%) as a colorless oil, which was fully characterized by ^{1}H NMR, ^{13}C NMR and IR spectroscopic analysis, and elemental analysis.

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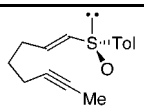
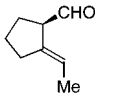
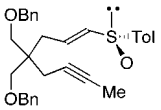
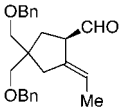
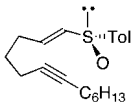
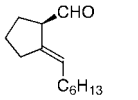
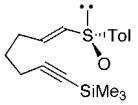
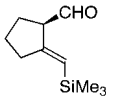
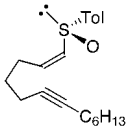
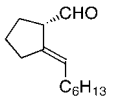
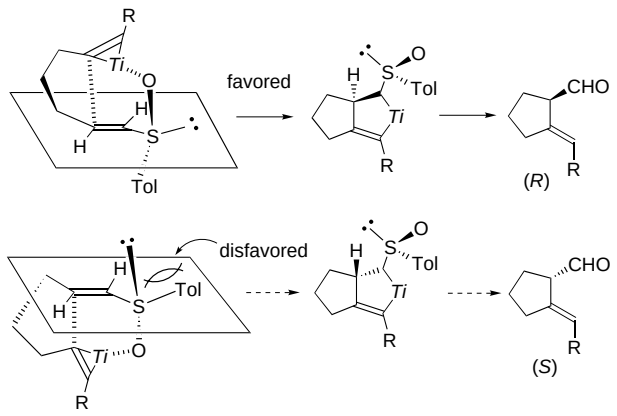
Table 2. Tandem cyclization and the Pummerer reaction of vinyl sulfoxides.

Entry	Enyne		Aldehyde[a]		Yield [%][b]	e.r.[c]
1		**20**		**24**	40[d] (60)	95:5
2		**21**		**25**	56 (66)	95:5
3		**17**		**18**	70,[e] 43[f] (74)	93:7
4		**22**		**26**	(62)[g]	92:8
5		**23**		**27**	(30)	79:21

[a] While the absolute configurations of **18** and **27** have been established, others were assigned by analogy, based on the sign of $[\alpha]_D$. [b] Yield isolated after purification. Values in parentheses were determined by ^{1}H NMR spectroscopic analysis of a crude sample with an internal standard. [c] Enantiomeric ratio was assessed after reduction to the alcohol [see Eq. (3)]. [d] The low yield may reflect the volatility of this compound. [e] This sample contains a small amount (ca. 10%) of unknown impurity. [f] Pure sample after repeated purification. [g] This aldehyde is very unstable and its attempted purification was not successful. Characterization was performed after reduction of crude **26** to the corresponding alcohol.



Scheme 1. Proposed reaction course from *E*,*R*-vinyl sulfoxides to *R*-aldehydes. *Ti* = Ti(O*i*Pr)$_2$.

The enantiomeric ratio was determined after derivatization to the alcohol **19**. $[\alpha]_D^{27} = -94.0$ ($c = 0.2$ in $CHCl_3$) for a sample of 93:7 enantiomeric ratio.

Typical procedure for **19** [Eq. (3)]: A crude sample of **18**, prepared from **17** (100 mg) as above, was reduced with sodium borohydride (10.4 mg, 0.174 mmol) in 6 mL of MeOH at 0 °C. After 10 min, the solution was allowed to warm to RT and was stirred for 1 h. After the addition of water and diethyl ether, the organic layer was separated, dried over Na_2SO_4, and concentrated to an oil. The crude product was chromatographed on silica gel to afford **19** (37.8 mg, 61% overall from **17**) as a colorless oil, which was fully characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopic analysis, and elemental analysis. The enantiomeric ratio was determined by the formation of the Mosher ester. $[\alpha]_D^{27} = -18.5$ ($c = 0.4$ in $CHCl_3$) for a sample of 93:7 enantiomeric ratio.

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[1] *Reagents for Organic Synthesis, Vols. 1–19*, Wiley, New York, **1967–1999**; *Encyclopedia of Reagents for Organic Synthesis, Vols. 1–8* (Ed.: L. A. Paquette), Wiley, New York, **1995**.

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[5] There is one report that deuteriolysis of an sp^3-carbon–metal bond of a certain zirconacycle proceeded with retention of configuration, which is consistent with the stereochemistry of the mechanism in Eq. (1). M. Mori, N. Uesaka, F. Saitoh, M. Shibasaki, *J. Org. Chem.* **1994**, *59*, 5643–5649.

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Tetrahedron **1994**, *50*, 6049 – 6060; R. W. Hoffmann, R. K. Dress, T. Ruhland, A. Wenzel, *Chem. Ber.* **1995**, *128*, 861 – 870; S. Nakamura, R. Nakagawa, Y. Watanabe, T. Toru, *Angew. Chem.* **2000**, *112*, 361 – 363; *Angew. Chem. Int. Ed.* **2000**, *39*, 353 – 355.

[7] Stereospecific transmission of the geometry of enynes to that of the metalated sp^3-carbon atom in the metallacycles [e.g. -CXY-Ti carbon atom in Eq. (1)] is an important issue for the stereoselective preparation of cyclic systems. As the resulting metalated sp^3-carbon atom, alkyl (refs. [6] and [7a–d]), allylic (ref. [7e]), benzylic (refs. [7b] and [7f]), and α-sulfenyl (this work) carbon atoms satisfied the above objective, but α-sulfonyl (this work) and α-alkoxycarbonyl (ref. [7d]) carbon atoms do not. For synthetic applications of the aforementioned stereodefined metallacycles, also see the following: a) S. F. Fillery, G. J. Gordon, T. Luker, R. J. Whitby, *Pure Appl. Chem.* **1997**, *69*, 633 – 638; b) Z. Zhao, Y. Ding, G. Zhao, *J. Org. Chem.* **1998**, *63*, 9285 – 9291; c) G. J. Gordon, T. Luker, M. W. Tuckett, R. J. Whitby, *Tetrahedron* **2000**, *56*, 2113 – 2129; d) H. Urabe, K. Suzuki, F. Sato, *J. Am. Chem. Soc.* **1997**, *119*, 10014 – 10027; e) H. Urabe, T. Takeda, D. Hideura, F. Sato, *J. Am. Chem. Soc.* **1997**, *119*, 11295 – 11305; f) E. Negishi, D. Choueiry, T. B. Nguyen, D. R. Swanson, *J. Am. Chem. Soc.* **1994**, *116*, 9751 – 9752; See also: g) F. A. Hicks, N. M. Kablaoui, S. L. Buchwald, *J. Am. Chem. Soc.* **1996**, *118*, 9450 – 9451.

[8] For reviews on the Pummerer reaction, see: A. Padwa, D. E. Gunn, Jr., M. H. Osterhout, *Synthesis* **1997**, 1353 – 1377; O. De Lucchi, U. Miotti, G. Modena in *Organic Reactions, Vol. 40* (Ed.: L. A. Paquette), Wiley, New York, **1991**, pp. 157 – 406; D. S. Grierson, H.-P. Husson in *Comprehensive Organic Synthesis, Vol. 6* (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, pp. 909 – 947.

[9] H. Urabe, T. Hamada, F. Sato, *J. Am. Chem. Soc.* **1999**, *121*, 2931 – 2932.

[10] H. Urabe, F. Sato in *Lewis Acids in Organic Synthesis, Vol. 2* (Ed.: H. Yamamoto), Wiley-VCH, Weinheim, **2000**, pp. 653 – 798.

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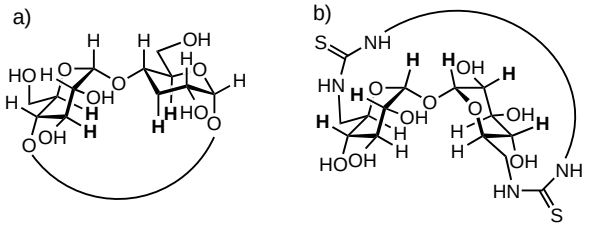
[12] The starting vinyl sulfoxides were prepared from a commercially available sample of homochiral methyl tolyl sulfoxide and assumed to retain the same level of *ee* values (see reference [11]). Thus, the enantiomeric ratios shown in Eq. (3) and Table 2 have not been corrected for the actual *ee* values of the vinyl sulfoxides.

Cyclotrehalins: Cyclooligosaccharide Receptors Featuring a Hydrophobic Cavity**

Juan M. Benito, José L. Jiménez Blanco, C. Ortiz Mellet,* and José M. García Fernández*

Dedicated to Dr. Jacques Defaye

Interactions between carbohydrates and other biomolecules play a prominent role in many biological recognition processes.[1] The complexity of such phenomena has stimulated the use of model systems to gather information about their nature (hydrophobic, polar, hydrogen bonds) and to unravel the factors influencing the binding specificity and the stability of carbohydrate-containing supramolecular entities.[2] Among sugar-derived model hosts, the commercially available cyclodextrins (CDs) have been by far the most extensively investigated for this purpose,[3] as they feature a hydrophobic cavity that can accommodate a guest molecule of appropriate size. The study of the resulting inclusion complex, by techniques such as NMR spectroscopy, is facilitated by the high symmetry and the rigidity of the CD structure. Yet, this strait-jacketed host has an intrinsic limitation: Exclusively contacts involving the inner α face of the D-glucopyranose units (i.e., H-3 and H-5) are observable (Scheme 1a).



Scheme 1. Representation of a) cyclodextrins (CDs) and b) trehalose cyclooligosaccharides (cyclotrehalins, CTs) incorporating thiourea intersaccharide bridges. The CH protons directed toward the inside of the corresponding cavities are in boldface.

Although much effort has been directed towards the preparation of synthetic CD analogues bearing a cavity of designed shape, size, and electrostatic potential,[4,5] no cyclooligosaccharide hosts suitable for the analysis of specific interactions involving the β face of the monosaccharides have been reported so far.

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