

Table 1. Structural parameters for H₁-platinum and platinum foil. CN = coordination number.

	Shell	CN	Dist. R [Å]	2σ ² [Å ²]	R factor [%]
H ₁ -Pt	Pt	7.0(1)	2.749(1)	0.0126(1)	24.2
	Pt	2.9(3)	3.893(6)	0.0177(9)	
	Pt	13.3(8)	4.795(4)	0.0220(7)	
	Pt	7.3(7)	5.466(5)	0.026(1)	
Pt foil	Pt	12	2.764(1)	0.0091(1)	22.0
	Pt	6	3.915(3)	0.0125(5)	
	Pt	24	4.808(2)	0.0143(3)	
	Pt	12	5.509(4)	0.0180(6)	

associated decrease in coordination numbers can be attributed to the presence of a high proportion of surface atoms. An additional effect of the larger number of surface atoms is an apparent shortening of the metal–metal bonds relative to those of the bulk metal.

A separate series of experiments employed lower surfactant concentrations in order to demonstrate that the structure of nanostructured H₁-Pt is a result of the liquid-crystalline phase acting as a template. Treating micellar solutions of C₁₆(EO)₈ [or cetyltrimethylammonium bromide (CTAB) as a cationic surfactant] and HCPA with iron as described above gave dense, unstructured particles. These results confirm that the template mechanism responsible for formation of M41S at low surfactant concentrations does not operate here.

The preparation of H₁-Pt is strongly dependent on the reducing agent. Hydrogenation (25 bar, 12 h) afforded only dendritic crystals, as revealed by TEM. Hydrogenation of the platinum salt is slower than reduction with iron or hydrazine and therefore allows the liquid-crystalline phase to reorganize, and large crystals to grow.

However, the confinement of the polar metal salt within the aqueous domains of the lyotropic phase does not imply that the same liquid-crystal template mechanism that is observed for the production of siliceous ceramic oxides^[1,2] is responsible for the development of the metal nanostructure. The primary product of the reduction, a cluster of platinum(0) atoms, cannot be stabilized by the liquid-crystalline environment in the same way as the oligomeric silicic acid precursor of silica, which is able to undergo hydrogen bonding. Furthermore, a large reduction in the product's volume relative to that of the low-density (with respect to Pt) precursor ion, has to be accounted for. This is also the reason why no monolithic material is formed during the reduction. As the lyotropic phase nevertheless acts as a structure-directing medium, it seems reasonable to assume that the metal is stabilized at the interface between the hydrophobic and the hydrophilic domains of the microphase-separated environment. Reduction of the platinum salt affords small colloidal primary particles at this interface. Subsequently, these primary particles agglomerate and coalesce, until a wall thickness is reached at which the structure is mechanically stable. The proposed mechanism can also explain why only fast reduction is able to generate a metal nanostructure; only then can the nanostructure be generated before the LC phase is able to rearrange. Metal nanoparticles stabilized at this interface in micellar block copolymer solutions have been observed before.^[1,3]

Our experiments demonstrate that lyotropic liquid-crystalline phases provide versatile reaction media for the synthesis of nanostructured mesoporous platinum. The inherent nanostructure of the porous material provides a high surface area, which is advantageous for catalytic applications. The large absolute particle size (relative to classical metal colloids) might allow for greater ease of catalyst without compromising the surface area.

The combination of high surface area with a tailored nanoarchitecture consisting of regular pores and a continuous electron-conduction pathway would be expected to be advantageous in fuel cells, batteries, or sensors, whose performance is determined by mass transport and interfacial processes.

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Asymmetric Aziridination over Ylides: Highly Stereoselective Synthesis of Acetylenyl-*N*-sulfonylaziridines**

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Although chiral aziridines have found numerous applications in the synthesis of many kinds of biologically important substances,^[1] development of simple but efficient methods for preparing them, especially the functionalized aziridines, is still a

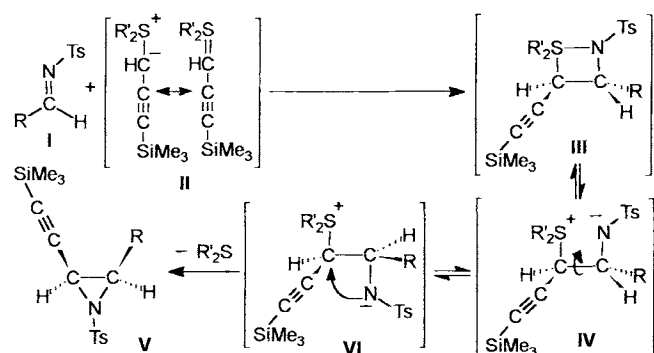
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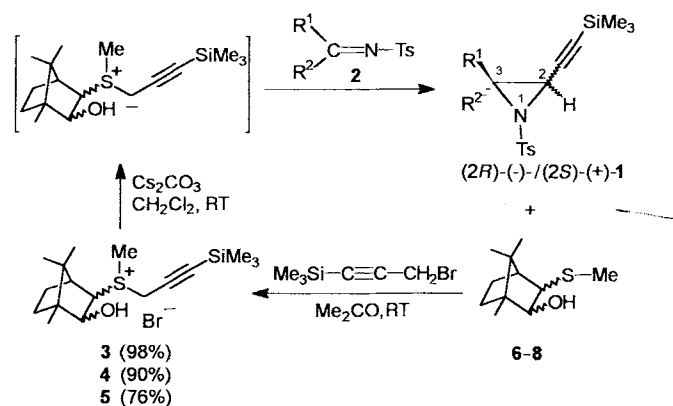
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great challenge. By retrosynthetic analysis, there are two direct pathways for constructing the nitrogen-containing three-membered ring: reaction of a nitrene with a prochiral C=C bond^[2-4] and of a carbene (or its equivalent carbanion or ylide) with a prochiral C=N bond.^[5-7] In contrast to the extensively studied and overwhelmingly successful asymmetric epoxidation^[8] and asymmetric cyclopropanation,^[9] asymmetric aziridination is much less explored. Most examples appeared in the 1990s.^[10] Evans et al.^[2a] and Jacobsen et al.^[2b] reported two excellent asymmetric aziridinations of a prochiral C=C bond with a nitrene in the presence of a chiral catalyst. Due to the intrinsic high reactivity of nitrenes, no aliphatic substrate was used in these reactions.^[11] By the other route, Jacobsen et al.^[5] realized the first asymmetric aziridination of a prochiral C=N bond with a carbene, and obtained a *cis/trans* mixture of chiral aziridines in low yields and moderate *ee* values. A substrate-controlled asymmetric aza-Darzens reaction with good *de* values was reported by Davis et al.^[6a] Very recently, Aggarwal et al.^[12] disclosed an efficient, asymmetric benzylidene transfer to a prochiral C=N bond by a catalytic ylide aziridination. Optically active aziridines were also prepared by methylene transfer from $\text{Me}_2\text{S}^+\text{CH}_2^-$ or $\text{Me}_2\text{S}(\text{O})^+\text{CH}_2^-$ to chiral sulfonimines.^[6c-e] We found that the ylide pathway provides very efficient entry to vinylaziridines^[13] and chiral epoxides.^[14] For vinylaziridines, a mixture of *cis/trans* isomers was always obtained. After numerous investigations, exclusive *cis* selectivity was achieved by the reaction of *N*-sulfonylimines with propargylic sulfonium ylides under phase-transfer conditions. This may be explained by an intermediate formed by the [2+2] cycloaddition of the imine and the ylide (Scheme 1). This is similar to the epoxidation reaction of carbonyl compounds with propargylic telluronium ylides.^[15] The high stereoselectivity enables us to realize a reagent-controlled asymmetric aziridination by a ylide route. We here disclose the preliminary results for preparing optically active acetylenylaziridines **1** in high yields and moderate to high *ee* values (Scheme 2).

Several results from the reaction of *N*-sulfonylimines **2** and sulfonium ylides—produced in situ from chiral sulfonium salts **3**, **4**, or **5**—under solid-liquid phase-transfer conditions are summarized in Table 1. This reaction proceeds smoothly with various kinds of substrates, including aryl- and heteroarylaldimines (reactions 4, 10, and 13), α,β -unsaturated



Scheme 1. Mechanism of the aziridination with propargylic sulfonium ylides. The [2+2] cycloaddition (II \rightarrow III) is the rate-determining step. Due to steric hindrance, only the *trans* product forms.



Scheme 2. Asymmetric aziridination with chiral sulfonium propargylides (yields are given in parentheses). Compounds **6-8** were retrieved after the reaction; **3**, **6** *exo-S*, *exo-OH*; **4**, **7** *endo-S*, *endo-OH*; **5**, **8** *endo-S*, *exo-OH*.

aldimines (reaction 5), aliphatic aldimines (reactions 6, 7, 11, and 14), and even relatively unreactive ketimine (reaction 8). It is especially noteworthy that aziridination succeeded in aliphatic aldimine and ketimine systems, which is not possible with the nitrene or carbene methods (see above).

There is one example of a chiral, sulfide-catalyzed asymmetric ylide aziridination.^[12] Although it gives high *ee* values and pro-

Table 1. Synthesis of chiral **1** by asymmetric aziridination of *N*-sulfonylimines **2** with sulfonium salts **3**, **4**, and **5**—derived from D-(+)-camphor—under phase-transfer conditions [a].

Reaction	R ¹	R ²	Yield [%][b]	<i>cis/trans</i> [c]	[α] _D ²⁰ [°] (acetone)	<i>ee</i> [%][d]	Config. at C2[g]
1	phenyl	H	85[h]	>99/1	-17.2 (<i>c</i> = 1.16)	50.5	<i>R</i> [f]
2	<i>p</i> -acetoxyphenyl	H	87[h]	>99/1	-12.0 (<i>c</i> = 1.20)	50.0	(<i>R</i>)
3	<i>p</i> -fluorophenyl	H	89[h]	>99/1	-28.4 (<i>c</i> = 1.07)	69.5(96.6[e])	(<i>R</i>)
4	3-pyridinyl	H	85[h]	>99/1	-20 (<i>c</i> = 1.35)	77.5(99.1[e])	(<i>R</i>)
5	<i>trans</i> -PhCH=CH	H	88[h]	>99/1	-13.7 (<i>c</i> = 1.00)	44.3	(<i>R</i>)
6	cyclohexyl	H	81[h]	>99/1	-21.1 (<i>c</i> = 0.67)	84.9	(<i>R</i>)
7	<i>tert</i> -butyl	H	92[h]	>99/1	-23.6 (<i>c</i> = 1.25)	40.8	(<i>R</i>)
8	Me	Me	95[h]	-	-79 (<i>c</i> = 1.04)	67.4	(<i>R</i>)
9	Phenyl	H	88[i]	>99/1	+8.8 (<i>c</i> = 1.00)	25.7	<i>S</i> [f]
10	3-pyridinyl	H	85[i]	>99/1	+13.3 (<i>c</i> = 0.80)	56.3	(<i>S</i>)
11	cyclohexyl	H	90[i]	>99/1	+10.6 (<i>c</i> = 0.40)	51.9	(<i>S</i>)
12	phenyl	H	89[j]	>99/1	+4.2 (<i>c</i> = 1.10)	14.0	(<i>S</i>)
13	3-pyridinyl	H	82[j]	>99/1	+8.8 (<i>c</i> = 0.80)	41.9	(<i>S</i>)
14	cyclohexyl	H	89[j]	>99/1	+8.7 (<i>c</i> = 0.50)	39.2	(<i>S</i>)

[a] All reactions were carried out with an imine:sulfonium salt:Cs₂CO₃ ratio of 1:1.2:1.2 on a 0.5 mmol scale in CH₂Cl₂ at room temperature. In all cases, chiral sulfides **6**, **7**, or **8** were recovered in >80% yields without loss of optical purity after work-up. [b] Yields of isolated products based on imines. [c] Determined by 300 MHz ¹H NMR analysis and/or HPLC. [d] Determined by chiral HPLC on a Chiralcel OD column or a Chiralpak AD column. [e] The *ee* values refer to those after single recrystallization. [f] Determined for one of the aziridine carbons connected to the acetylenyl group by transforming the product into a compound whose configuration was known: *cis*-2-methoxycarbonyl-3-phenyl-*N*-tosylaziridine [6a]. [g] The configuration in parentheses was estimated by comparison with the corresponding phenyl analog. [h] Salt **3**. [i] Salt **4**. [j] Salt **5**.

ceeds in a catalytic mode, it requires strict reaction conditions and suffers from low *trans/cis* selectivity ($\approx 3/1$). The present asymmetric aziridination is a stoichiometric reaction but may represent a promising general^[16] and practical approach to optically active functionalized aziridines due to its compatibility to a wide range of substrates, high yields, and very mild reaction conditions. Furthermore, the ylide precursors (chiral sulfides) could be easily recovered in higher than 80% yields without loss of optical purity and reused. Though the *ee* value of the product is not very high (maximum 84.9%, reaction 6), it can be efficiently improved by a single recrystallization from *n*-hexane; this may offer a practical utility of these products. For example, the *ee* values of the products from reactions 3 and 4 can be increased from 69.5% to 96.6% and from 77.5% to 99.1% for yields of 58% and 52%, respectively. The opposite asymmetric induction was achieved with sulfonium salts containing *exo*-sulfido groups (**3**, reactions 1-8) to provide (*2R*)-(-)-aziridines and *endo*-sulfido groups^[17] (**4** and **5**, reactions 9-14) to provide (*2S*)-(+)-aziridines. Chiral acetylenylaziridines are very difficult to prepare by the two direct approaches based on carbene, nitrene, or aza-Darzens reaction.^[18]

Experimental Section

General procedure for aziridination: **2** (0.5 mmol), the chiral sulfonium salt **3**, **4**, or **5** (0.6 mmol), and Cs₂CO₃ (0.6 mmol) were mixed and stirred in CH₂Cl₂ (3 mL, reagent grade, used directly without drying) at room temperature in air. After the reaction was completed (TLC, 2–5 h), the reaction mixture was filtered through a short silica-gel column to remove inorganic salts. The filtrate was concentrated and purified by chromatography on a silica-gel column with petroleum ether (60–90 °C) and ethyl acetate (4/1) as the eluent to give pure (-) or (+) *N*-sulfonyl acetylenylaziridines **1**. Chiral sulfides **6**, **7**, or **8** were also recovered (> 80% yields).

3, **4**, or **5**: A mixture of a chiral sulfide [14] **6**, **7**, or **8** (2.004 g, 10 mmol) and 3-trimethylsilylpropargyl bromide [19] (2.294 g, 12 mmol) in acetone (3 mL) was stirred at room temperature for 6–48 h. Most of acetone was removed under reduced pressure, and the residue collected by filtration, washed with dry ether (3 × 40 mL), and dried under vacuum at room temperature to give the desired sulfonium salt as a white solid. It was used directly without further purification.

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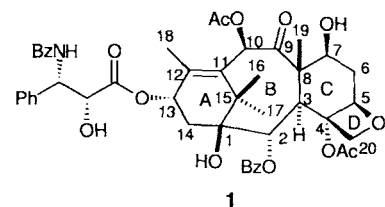
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Synthesis of Taxoid Ring Systems: AC → ABC Approach by Way of Intramolecular Alkylation**

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Taxol (**1**) is an attractive molecular target both in terms of its biological activity and its synthetic complexity, which includes a conformationally restricted ABCD ring system bearing many stereogenic centers with interesting functional groups.^[1–3] We have focused on the development of a method for constructing the B ring of the taxoid system.^[4] There are several methods for the preparation of medium-membered rings, however, it has been difficult to effect direct cyclization of eight-membered rings due to entropic and enthalpic effects.^[5] This is especially true, if the conformation of the desired cyclic molecule is restricted in a highly strained conformation, such as in the taxoid system, thereby making the preparation of the ring from a strain-free acyclic compound even more difficult. We have previously reported several methods for overcoming this problem; for example, the contraction of large-membered ring molecules and the intramolecular alkylation of cyanohydrin ethers with alkyl iodides, tosylates, and allylic halides, efficiently form 10-



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