knowledge $SnSe_2\{Co(\eta\text{-}C_5H_5)_2\}_{0.33}$ has the highest reported T_c for an organometallic intercalate.

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Enantioselective Synthesis of a Chiral Intermediate for Aztreonam and Related Monobactam Antibiotics

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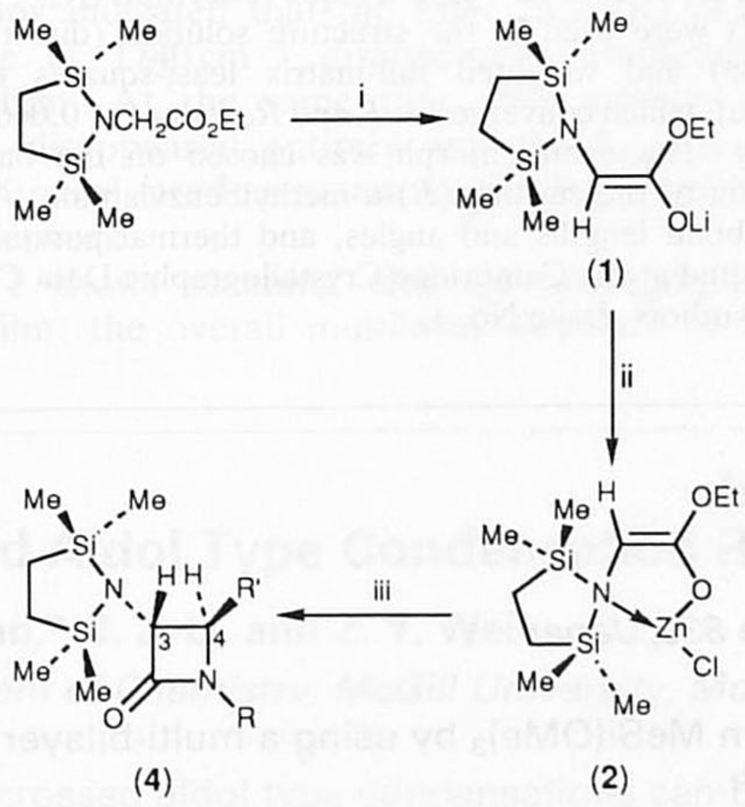
The enantioselective synthesis of *trans*-(3*R*,4*S*)-1-(*R*)-α-methylbenzyl-3-(2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl)-4-*N*-(*R*)-α-methylbenzyliminoazetidin-2-one has been accomplished by reaction of the chlorozinc enolate of an *N,N*-diprotected glycine ethyl ester with a chiral α-diimine.

Recently, we have demonstrated that zinc enolates of disubstituted glycine esters are effective reagents for the diastereoselective synthesis of 3-amino-2-azetidinones, the principal building blocks for the synthesis of aztreonam and related monobactam antibiotics.[1] Whereas most studies in the field of β-lactam synthesis have dealt with the development of enantioselective routes to chiral intermediates for thienamycin and related antibiotics,[2,3] little attention has been paid to the enantioselective synthesis of 3-aminoazetidin-2-ones.[4]



a; R = Bu^t, R' = C(H)=N–R
b; R = (*R*)-C(H)(Me)Ph, R' = C(H)=N–R
c; R = (*R*)-C(H)(Me)Ph, R' = 2–pyridyl

Scheme 1. *Reagents and conditions*: i, lithium diamide (LDA) in THF, −78 °C; ii, $ZnCl_2$ in Et_2O, −78 °C; iii, R–N=C(H)–R′ (**3**), THF, −78 °C → room temperature.

Here we report the first enantioselective zinc-mediated synthesis of *trans*-(3*R*,4*S*)-1-(*R*)-α-methylbenzyl-3-(2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl)-4-*N*-(*R*)-α-methylbenzyliminoazetidin-2-one starting from *N,N*′-bis(*R,R*′)-α-methylbenzyl-1,4-diazabuta-1,3-diene [(*R*)-α-methylbenzyl-DAB].[5]

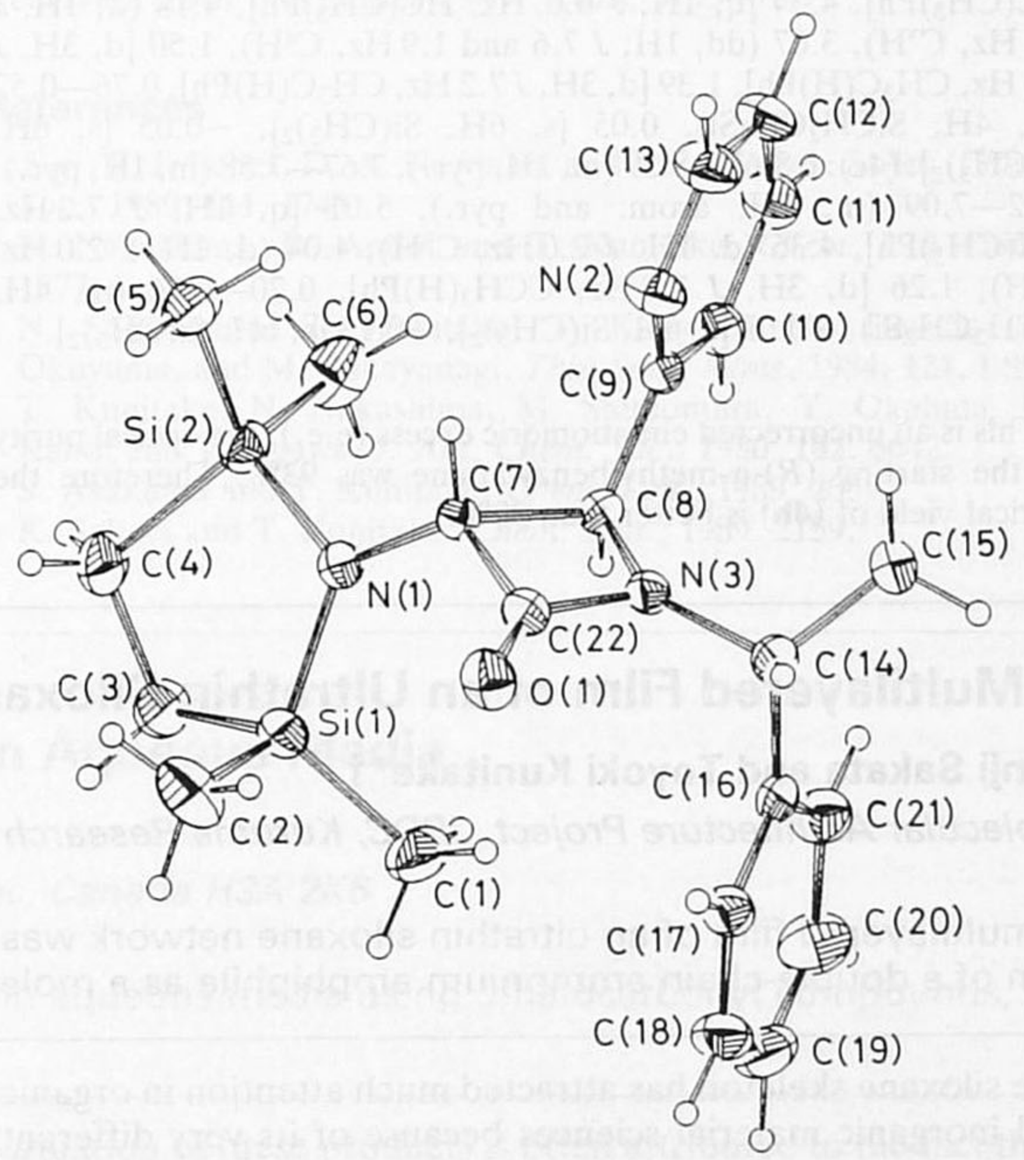


Figure 1. An ORTEP drawing (30% probability level) of *trans*-(3*R*,4*S*)-1-(*R*)-α-methylbenzyl-3-(2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl)-4-(2-pyridyl)azetidin-2-one (**4c**) together with the adopted numbering scheme.

We were interested in the reactions of zinc enolates with 1,4-disubstituted 1,4-diazabuta-1,3-dienes [(*R*)-DAB] to form 3-amino-4-imino-β-lactams because the 4-imino group represents a protected aldehyde function, which is suitable for further derivatisation.[6] These reactions, which display a very high diastereoselectivity (Scheme 1), surprisingly proceeded also with a high enantioselectivity using the easily available (*R*)-α-methylbenzyl-DAB. Thus the zinc enolate (**2**) was prepared *in situ*,[1] and reacted with t-butyl-DAB (**3a**) or (*R*)-α-methylbenzyl-DAB (**3b**) in tetrahydrofuran (THF) at −70 °C to afford *trans*-1-t-butyl-3-(2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl)-4-*N*-t-butyliminoazetidin-2-one (**4a**)† in 98% yield and *trans*-(3*R*,4*S*)-1-(*R*)-α-methylbenzyl-3-(2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl)-4-*N*-(*R*)-α-methylbenzyliminoazetidin-2-one (**4b**)† in 90% chemical and 86% optical‡ yields respectively. The latter compound is a threefold protected intermediate for the synthesis of aztreonam and related monobactam antibiotics.

Zinc enolate (**2**) also reacted smoothly with *N*-(*R*)-α-methylbenzyl(2-pyridyl)carbaldimine (**3c**), a chiral imine containing a 1,4-diazabuta-1,3-diene skeleton, to afford *trans*-(3*R*,4*S*)-1-(*R*)-α-methylbenzyl-3-(2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentyl)-4-(2-pyridyl)azetidin-2-one (**4c**)† in 98% chemical and ≥95% optical yield. The absolute configuration of (**4c**) and therefore also of (**4b**) was determined to be 3*R*,4*S* from an *X*-ray structure determination,§ the result of which is shown in Figure 1.

The reactions of zinc enolate (**2**) with (*R*)-DAB substrates proved to be superior to those of the corresponding lithium enolate (**1**) under the same reaction conditions. Starting from the latter enolate (**1**) compound (**4a**) was produced in only 15% yield, (**4b**) in 45% chemical and 40% optical yield, and (**4c**) in 70% chemical and 50% optical yield. A discussion on the difference in reactivity of lithium and zinc enolates will be presented in a forthcoming paper.

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† The new compounds (**4**) gave IR and ^{1}H and ^{13}C NMR spectra and elemental analyses consistent with the assigned structures. 200 MHz ^{1}H NMR($CDCl_3$) (**4a**): δ 7.46 (d, 1H, *J* 7.8 Hz, HC=N), 4.00 (d, 1H, *J* 1.8 Hz, C^{3}H), 3.82 (dd, 1H, *J* 7.8 and 1.8 Hz, C^{4}H), 1.31 [s, 9H, $C(CH_3)_3$], 1.21 [s, 9H, $C(CH_3)_3$], 0.78—0.61 (m, 4H, $SiCH_2CH_2Si$), 0.12 [s, 6H, $Si(CH_3)_2$], 0.09 [s, 6H, $Si(CH_3)_2$]. (**4b**): δ 7.53 (d, 1H, *J* 7.6 Hz, HC=N), 7.41—7.13 (m, 10H, arom.), 4.85 [q, 1H, *J* 7.2 Hz, $HC(CH_3)Ph$], 4.34 [q, 1H, *J* 6.6. Hz, $HC(CH_3)Ph$], 4.18 (d, 1H, *J* 1.9 Hz, C^{3}H), 3.67 (dd, 1H, *J* 7.6 and 1.9 Hz, C^{4}H), 1.50 [d, 3H, *J* 6.6 Hz, $CH_3C(H)Ph$], 1.39 [d, 3H, *J* 7.2 Hz, $CH_3C(H)Ph$], 0.76—0.52 (m, 4H, $SiCH_2CH_2Si$), 0.05 [s, 6H, $Si(CH_3)_2$], −0.05 [s, 6H, $Si(CH_3)_2$]. (**4c**): δ 8.62—8.59 (m, 1H, pyr.), 7.67—7.58 (m, 1H, pyr.), 7.32—7.09 (m, 7H, arom. and pyr.), 5.01 [q, 1H, *J* 7.2 Hz, $CH(CH_3)Ph$], 4.36 (d, 1H, *J* 2.0 Hz, C^{3}H), 4.04 (d, 1H, *J* 2.0 Hz, C^{4}H), 1.26 [d, 3H, *J* 7.2 Hz, $CCH_3(H)Ph$], 0.70—0.56 (m, 4H, $SiCH_2CH_2Si$), −0.09 [s, 6H, $Si(CH_3)_2$], −0.13 [s, 6H, $Si(CH_3)_2$].

‡ This is an uncorrected enantiomeric excess (e.e.); the optical purity of the starting (*R*)-α-methylbenzylamine was 93%. Therefore the optical yield of (**4b**) is better than 90%.

§ *Crystal data* for (**4c**): $C_{22}H_{31}N_3OSi_2$, *M* = 409.68, monoclinic, space group *I*2, *a* = 18.410(1), *b* = 6.813(1), *c* = 19.471(1) Å, β = 105.77(1)°, *U* = 2350.3(4) Å^3, *Z* = 4, *F*(000) = 880, D_c = 1.158 g cm^{-3}, *T* = 295 K, Mo-K_α (Zr-filtered) radiation (λ = 0.71073 Å), μ(Mo-K_α) = 1.40 cm^{-1}. A redundant set of 6910 reflections was collected on an Enraf-Nonius CAD4F diffractometer in the range 2.7 ≤ 2θ ≤ 55°. 2195 Unique reflections (R_{av} = 0.04) with $I \geq 2.5\sigma(I)$ were used in the structure solution (direct methods; SHELXS-86) and weighted full-matrix least-squares refinement (SHELX-76), which converged at *R* and R_w values of 0.046 and 0.044 respectively. The enantiomorph was chosen on the basis of the configuration of the starting (*R*)-α-methylbenzylamine. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

A Multilayered Film of an Ultrathin Siloxane Network

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A multilayered film of an ultrathin siloxane network was prepared from $MeSi(OMe)_3$ by using a multi-bilayer cast film of a double-chain ammonium amphiphile as a molecular template.

The siloxane skeleton has attracted much attention in organic and inorganic material sciences because of its very different structures. The control of the siloxane skeleton on the molecular scale is a central problem in this field.[1] We report the preparation of siloxane networks with molecular-scale thickness.

Owing to their remarkable self-assembling properties, synthetic bilayer membranes can be transformed into free-

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