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Synthesis and enantioselective enzymatic hydrolysis of *rac*-dimethylphenyl[1-(phenylacetamido)ethyl]silane

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Abstract

Racemic dimethylphenyl[1-(phenylacetamido)ethyl]silane [*rac*-**5**] has been made by a four-step synthesis starting from (chloromethyl)dimethylphenylsilane [$PhMe_2SiCH_2Cl$ (**1**) → $PhMe_2SiCH(Cl)Me$ (*rac*-**2**) → $PhMe_2SiCH(I)Me$ (*rac*-**3**) → $PhMe_2SiCH(NH_2)Me$ (*rac*-**4**) → $PhMe_2SiCH[N(H)C(O)CH_2Ph]Me$ (*rac*-**5**); total yield 41%]. Enantioselective enzymatic hydrolysis of *rac*-**5**, catalyzed by immobilized penicillin G acylase (E.C. 3.5.1.11) from *Escherichia coli* 5K (pHM 12), gave (*R*)-(1-aminoethyl)dimethylphenylsilane [(*R*)-**4**] in 40% yield with an enantiomeric purity of 92% ee.

Introduction

During our investigations on the synthesis of optically active organosilicon compounds by use of stereoselective biotransformations, both whole microbial cells [1–6] and free enzymes [7] were used as biocatalysts (for recent reviews see refs. 8–10). The types of reactions studied so far comprise enantioselective reductions, ester hydrolyses, and transesterifications. We report here the enzymatic synthesis of (*R*)-(1-aminoethyl)dimethylphenylsilane [(*R*)-**4**] starting from racemic dimethylphenyl[1-(phenylacetamido)ethyl]silane (*rac*-**5**). The optically active (1-aminoethyl)silane (*R*)-**4** was obtained by a kinetic resolution of *rac*-**5** using immobilized penicillin G acylase (PGA, E.C. 3.5.1.11) from *Escherichia coli* 5K (pHM 12) as biocatalyst (for a preliminary report on this reaction, see ref. 11). This type of enzymatic reaction (amide hydrolysis) has not previously been used for the preparation of optically active organosilicon compounds.

Results and discussion

Synthesis of rac-*5*

Compound *rac*-**5** was made by a four-step route starting from (chloromethyl)dimethylphenylsilane (**1**), as outlined in Scheme 1. Following a procedure described in

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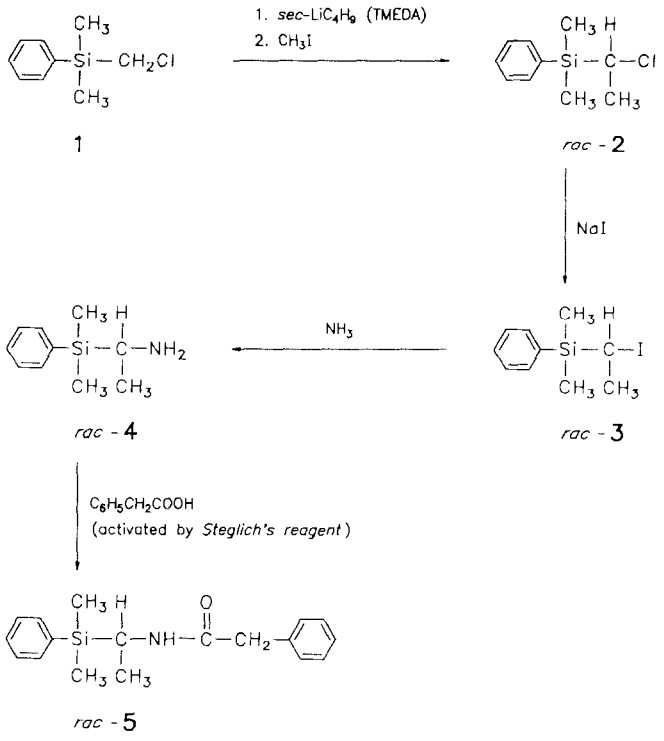


1 rac-2 rac-3 rac-4 rac-5

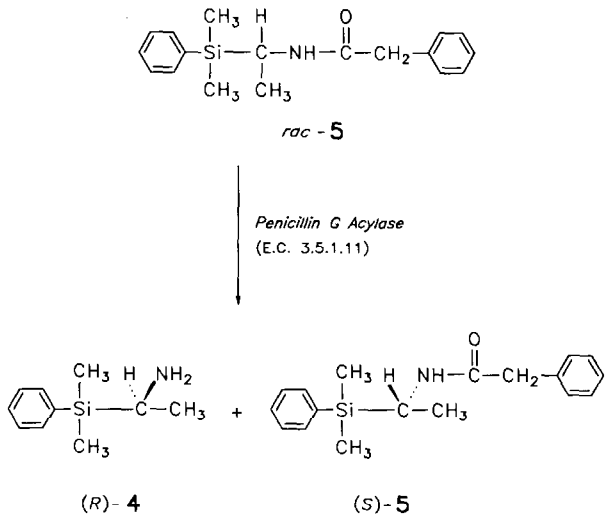
Scheme 1.

ref. 12 (in this context, see also refs. 13–15), the (chloromethyl)silane **1** was deprotonated by treatment with sec-butyllithium/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine in tetrahydrofuran to give [chloro(dimethylphenylsilyl)methyl]lithium, which when treated with methyl iodide gave the (1-chloroethyl)silane *rac*-**2** (yield 66%). Treatment of *rac*-**2** with sodium iodide in acetone (cf. ref. 16) gave the (1-iodoethyl)silane *rac*-**3** (yield 81%; ref. 16: 78%), which was then converted into the corresponding (1-aminoethyl)silane *rac*-**4** by reaction with ammonia under pressure, following a procedure described in ref. 16. Under optimized reaction conditions (see Experimental section), *rac*-**4** was obtained in 94% yield (ref. 16: 23–62%). In the last step, the [1-(phenylacetamido)ethyl]silane *rac*-**5** was prepared by acylation of *rac*-**4** with phenylacetic acid using 4,6-diphenylthieno[3,4-d]-1,3-dioxol-2-one 5,5-dioxide (Steglich's reagent [17–19]) as carboxyl activating agent (yield 82%).

The silane *rac*-**5** was synthesized for the first time (total yield 41%, based on **1** used). The precursors *rac*-**2**–*rac*-**4** have been described previously [16], but in the present paper a new method for the preparation of *rac*-**2** is described, as are optimized procedures for the synthesis of *rac*-**3** and *rac*-**4**.

Enzymatic hydrolysis of rac-*5*

Preliminary experiments have shown that (*R*)-**4** can be prepared by enantioselective hydrolysis of *rac*-**5** with immobilized PGA as biocatalyst (Scheme 2). The conditions for this bioconversion were optimized by analytical-scale studies [11], on



Scheme 2.

the basis of which the following conditions were chosen for a conversion of *rac*-**5** on a preparative scale (225 mg scale): 1.8 l of 0.1 *M* potassium phosphate buffer/dimethyl sulfoxide (99.5/0.5, v/v) as reaction medium, pH 7.5, temperature 37 °C, substrate concentration 0.42 mmol/l, 90 g immobilized PGA [100 U/g, related to the hydrolysis of penicillin G; acrylic beads (Eupergit C)], reaction time 3 hours (about 45% conversion of *rac*-**5**). After termination of the enzymatic hydrolysis by addition of ethyl acetate, the product (*R*)-**4** was separated from the unchanged substrate and isolated in 40% yield (related to *rac*-**5**) with an enantiomeric purity of 92% ee. The unchanged starting material (*S*)-**5** was recovered in 50% yield (related to *rac*-**5**).

The absolute configuration and enantiomeric purity of the product (*R*)-**4** were determined, after derivatization with (*S*)-α-methoxy-α-trifluoromethylphenylacetic acid [(*S*)-MTPA], by ^{1}H NMR spectroscopic studies (see ref. 20) and GLC, respectively. For comparison, a 1:1 mixture of the diastereomeric [(*S*)-MTPA] amides of (*R*)-**4** and (*S*)-**4** was prepared from *rac*-**4**. These amides were obtained by reaction of **4** with (*S*)-MTPA in the presence of *N*,*N*′-dicyclohexylcarbodiimide and a catalytic amount of (4-dimethylamino)pyridine.

The results described here demonstrate that enantioselective biotransformations, with immobilized enzymes as biocatalyst, may be useful for the synthesis of optically active organosilicon compounds on a preparative scale.

Experimental

(a) Chemical syntheses

All reactions were performed in dried solvents under dry nitrogen. Melting points were determined with a Reichelt Thermovar apparatus (without correction). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer operating at 400.1 and 100.6 MHz, respectively. Chemical shifts (ppm) were measured relative to the internal standard $Si(CH_3)_4$ (^{1}H and ^{13}C, δ 0). Assignment of the ^{13}C data was

assisted by DEPT experiments. ^{19}F and ^{29}Si NMR spectra were recorded on a Bruker AC-200 spectrometer operating at 188.3 and 39.8 MHz, respectively. Chemical shifts (ppm) were measured with respect to those of $CFCl_3$ (^{19}F, δ 0) or $Si(CH_3)_4$ (^{29}Si, δ 0) as external standard. Mass spectra were obtained with a Finnigan MAT 8430 mass spectrometer (EI MS, 70 eV); the *m/z* values given refer to the isotopes ^1H, ^{12}C, ^{14}N, ^{16}O, ^{28}Si, ^{35}Cl and ^{127}I.

*(Chloromethyl)dimethylphenylsilane (**1**)*
Synthesis according to ref. 14.

rac-*(1-Chloroethyl)dimethylphenylsilane* (rac-**2**)
A 1.4 *M* solution (164 ml) of sec-butyllithium in cyclohexane/isopentane (92/8, v/v; 0.23 mol sec-butyllithium) and 24.1 g (0.21 mol) *N,N,N′,N′*-tetramethylethylenediamine were successively added dropwise to a stirred solution of 40.0 g (0.217 mol) **1** in 260 ml of THF at −78°C during periods of 1.5 h and 20 min, respectively. After 1 h stirring at −78°C the mixture was allowed to warm to −55°C and a solution of 41.2 g (0.29 mol) of methyl iodide in 70 ml of THF was added dropwise during 1 h. When the addition was complete, stirring was continued for 40 min at −40°C and an additional 16 h at room temperature. The mixture was then added carefully (ice cooling) to 700 ml of saturated aqueous NH_4Cl. The organic phase was separated and the aqueous layer extracted three times with 350 ml portions of diethyl ether. The combined organic extracts were washed with water and dried over Na_2SO_4, and the solvent was then removed *in vacuo* and the residue fractionally distilled to yield 28.3 g (66%) of a colourless liquid, b.p. 76°C/6 Torr (ref. 16: b.p. 90–97°C/4 Torr). ^1H NMR ($CDCl_3$): δ 0.40 (s, 3H; $SiCH_3$), 0.41 (s, 3H; $SiCH_3$), 1.46 (d, ^3J(HH) 7.6 Hz, 3H; CCH_3), 3.53 (q, ^3J(HH) 7.6 Hz, 1H; SiCH(Cl)C), 7.4–7.6 (m, 5H; SiC_6H_5). ^{13}C NMR ($CDCl_3$): δ −6.1 ($SiCH_3$), −5.0 ($SiCH_3$), 20.1 (CCH_3), 45.0 ($SiCH(Cl)C$), 127.9 (C_m, SiC_6H_5), 129.6 (C_p, SiC_6H_5), 134.2 (C_o, SiC_6H_5), 135.7 (C_i, SiC_6H_5). MS: *m/z* 198 (1%, M^+), 135 (100%, $M^+ - CH(Cl)CH_3$). Anal. Found: C 60.4; H 7.5. $C_{10}H_{15}ClSi$ (198.8) calc.: C 60.43; H 7.61%.

rac-*(1-Iodoethyl)dimethylphenylsilane* (rac-**3**)
The procedure was as described in ref. 16. Sodium iodide (83.9 g; 0.56 mol) was added to a solution of 40.0 g (0.20 mol) *rac*-**2** in 200 ml of acetone and the mixture was stirred under reflux for 11 days. It was then cooled to room temperature, 200 ml of water were added and the mixture extracted three times with 250 ml portions of diethyl ether. The combined organic extracts were dried over Na_2SO_4, the solvent was removed *in vacuo*, and the residue fractionally distilled to yield 47.4 g (81%) of a colourless liquid, b.p. 66°C/0.2 Torr (ref. 16: yield 78%, b.p. 130°C/10 Torr). ^1H NMR ($CDCl_3$): δ 0.49 (s, 6H; $SiCH_3$), 1.83 (d, ^3J(HH) 7.8 Hz, 3H; CCH_3), 3.41 (q, ^3J(HH) 7.8 Hz, 1H; SiCH(I)C), 7.4–7.6 (m, 5H; SiC_6H_5). ^{13}C NMR ($CDCl_3$): δ −5.0 ($SiCH_3$), −3.1 ($SiCH_3$), 11.7 (CCH_3), 22.2 ($SiCH(I)C$), 127.9 (C_m, SiC_6H_5), 129.6 (C_p, SiC_6H_5), 134.1 (C_o, SiC_6H_5), 135.8 (C_i, SiC_6H_5). MS: *m/z* 290 (2%, M^+), 135 (100%, $M^+ - CH(I)CH_3$). $C_{10}H_{15}ISi$ (290.2).

rac-*(1-Aminoethyl)dimethylphenylsilane* (rac-**4**)
The procedure was a modification of that described in ref. 16. A 250 ml glass tube charged with 12.1 g (41.7 mmol) *rac*-**3** and ca. 180 ml of liquid ammonia was

placed in a 250 ml autoclave. When the autoclave was heated to 135 °C a pressure of 70–75 bar was reached. The autoclave was kept for 2.5 h under these conditions and then allowed to cool to room temperature. After evaporation of the excess of ammonia, 30 ml of a 6 *N* aqueous NaOH solution were added and the mixture was extracted four times with 70 ml portions of diethyl ether. The combined organic layers were dried over Na_2SO_4, the solvent was removed *in vacuo*, and the residue (consisting of a mixture of a white solid and a colourless oil) was fractionally distilled to yield 7.00 g (94%) of a colourless liquid, b.p. 82 °C/0.1 Torr (ref. 16: yield 23–62%, b.p. 90–130 °C/2 Torr), which partly crystallized at room temperature, to give a solid of m.p. 44–51 °C. ^{1}H NMR ($CDCl_3$): δ 0.32 (s, 3H; $SiCH_3$), 0.33 (s, 3H; $SiCH_3$), 1.15 (d, ^3J(HH) 7.4 Hz, 3H; CCH_3), 2.39 (broad 's', 2H; NH_2), 2.53 (q, ^3J(HH) 7.4 Hz, 1H; SiCH(N)C), 7.3–7.6 (m, 5H; SiC_6H_5). ^{13}C NMR ($CDCl_3$): δ −5.9 ($SiCH_3$), −5.6 ($SiCH_3$), 19.6 (CCH_3), 36.0 ($SiCH(N)C$), 127.9 (C_m, SiC_6H_5), 129.2 (C_p, SiC_6H_5), 134.1 (C_o, SiC_6H_5), 136.9 (C_i, SiC_6H_5). ^{29}Si NMR ($CDCl_3$): −0.4. MS: *m/z* 179 (3%, M^+), 44 (100%, $H_2N{=}C(CH_3)H^+$). $C_{10}H_{17}NSi$ (179.3).

rac-*Dimethylphenyl[1-(phenylacetamido)ethyl]silane* (rac-**5**)

A mixture of 1.00 g (3.06 mmol) 4,6-diphenylthieno[3,4-d]-1,3-dioxol-2-one 5,5-dioxide (Steglich's reagent), 0.41 g (3.01 mmol) phenylacetic acid and 0.24 g (3.03 mmol) pyridine in 25 ml of dichloromethane was stirred for 2 h at room temperature. Subsequently, 0.31 g (3.06 mmol) triethylamine were added, the solution turning orange-red. After 10 min stirring, a solution of 0.45 g (2.51 mmol) *rac*-**4** in 15 ml of dichloromethane was added dropwise. Stirring was continued for 2 h, giving a yellow solution. The mixture was extracted twice with 30 ml portions of 20% aqueous citric acid, three times with 50 ml portions of saturated aqueous $NaHCO_3$ solution, then again with 30 ml of 20% aqueous citric acid solution, and finally with 30 ml of water. The organic layer was dried over $MgSO_4$ and the solvent removed *in vacuo*. Recrystallization of the remaining solid from acetonitrile at −20 °C gave 0.61 g (82%) of white needles, m.p. 85 °C. ^{1}H NMR ($CDCl_3$): δ 0.19 (s, 3H; $SiCH_3$), 0.24 (s, 3H; $SiCH_3$), 1.02 (d, ^3J(HH) 7.5 Hz, 3H; CCH_3), 3.39 and 3.54 (AB system, ^2J(HH) 15.9 Hz, 2H; CCH_2C), 3.73 (dq, ^3J(HH) 7.5 Hz, ^3J(HH) 9.6 Hz, 1H; SiCH(N)C), 5.0–5.1 (m, 1H; NH), 7.1–7.4 (m, 10H; SiC_6H_5, CC_6H_5). ^{13}C NMR ($CDCl_3$): δ −5.4 ($SiCH_3$), 16.4 (CCH_3), 34.4 ($SiCH(N)C$), 44.1 (CCH_2C), 127.3, 128.0, 129.0, 133.8, 135.1 and 135.6 (SiC_6H_5, CC_6H_5), 170.3 (CO). ^{29}Si NMR ($CDCl_3$): δ −1.7. MS: *m/z* 297 (56%, M^+), 135 (100%, $M^+ - CH[N(H)C(O)CH_2C_6H_5]CH_3$). Anal. Found: C 72.7; H 7.9; N 4.7. $C_{18}H_{23}NOSi$ (297.5) calc.: C 72.68; H 7.79; N 4.71%.

Preparation of the [(S)-MTPA] amides of **4**, *determination of their absolute configuration, and their separation by gas chromatography*

A solution of 9.0 mg (50 μmol) **4** (chemically prepared racemic **4** or the biotransformation product **4**) in 0.5 ml dichloromethane was added at room temperature to a stirred mixture of 14.1 mg (60 μmol) (*S*)-α-methoxy-α-trifluoromethylphenylacetic acid [(*S*)-MTPA], 18.6 mg (90 μmol) *N,N'*-dicyclohexylcarbodiimide and 1–2 mg (4-dimethylamino)pyridine in 4 ml of dichloromethane. Stirring was continued until the reaction was complete [monitored by thin-layer chromatography (pre-coated plastic-backed plates, silica gel 60 F_{254}, Merck 5735; dichloro-

methane/diethyl ether (1/1, v/v)]. The suspension was centrifuged and the supernatant liquid isolated with a syringe and the solvent evaporated *in vacuo*. The residue was purified by preparative layer chromatography [pre-coated glass plates, silica gel 60, Merck 13895; dichloromethane/diethyl ether (1/1, v/v)]. The resulting mixture of the diastereomeric [(*S*)-MTPA] amides of (*R*)-**4** and (*S*)-**4** was dissolved in benzene-d_6 and then analyzed by NMR spectroscopy. The absolute configuration of the Si–C*H(NHR)–C skeleton of the [(*S*)-MTPA] amides of (*R*)-**4** and (*S*)-**4** was assigned by the correlation method described in ref. 20.

[(S)-MTPA] amide of (R)-4. ^{1}H NMR (C_6D_6: δ 0.15 (s, 3H; $SiCH_3$), 0.21 (s, 3H; $SiCH_3$), 0.91 (d, ^3J(HH) 7.5 Hz, 3H; CCH_3), 3.00 (q, ^5J(HF) 1.5 Hz, 3H; OCH_3), 3.84 (q, ^3J(HH) 7.5 Hz, 1H; SiC*H*(N)C), 6.3–6.4 (m, 1H; NH), 7.0–7.7 (m, 10H; SiC_6H_5, CC_6H_5). ^{19}F NMR (C_6D_6): δ −68.7.

[(S)-MTPA] amide of (S)-4. ^{1}H NMR (C_6D_6: δ 0.10 (s, 3H; $SiCH_3$), 0.11 (s, 3H; $SiCH_3$), 0.97 (d, ^3J(HH) 7.5 Hz, 3H; CCH_3), 3.05 (q, ^5J(HF) 1.6 Hz, 3H; OCH_3), 3.78 (q, ^3J(HH) 7.5 Hz, 1H; SiC*H*(N)C), 6.2–6.3 (m, 1H; NH), 7.0–7.7 (m, 10H; SiC_6H_5, CC_6H_5). ^{19}F NMR (C_6D_6): δ −68.9.

For separation of the [(*S*)-MTPA] amides of **4** by gas chromatography a Chrompack instrument (model 436) was used [capillary column Cp-Sil-5 CB, 10 m, 0.25 mm; split injection, 270 °C; carrier gas hydrogen; temperature programmme 150–200 °C (6 °/min); FID, 300 °C; retention time 3.7 (derivative of (*S*)-**4**) and 4.0 min, respectively (derivative of (*R*)-**4**)]. The samples used for these GLC studies were obtained as follows: After derivatization of chemically or enzymatically prepared **4** with (*S*)-MTPA by the procedure described above, the resulting reaction mixture was centrifuged and 1 µl of the supernatant was analyzed directly without further purification.

(b) Bioconversion

Immobilized penicillin G acylase (90 g; 9000 U, related to the hydrolysis of penicillin G) from *Escherichia coli* 5 K (pHM 12) [E.C. 3.5.1.11; immobilized on Eupergit C (Röhm, Germany)] was suspended at 37 °C in 1.8 l of 0.1 *M* potassium phosphate buffer (pH 7.5). The reaction was started by adding a solution of 225 mg (756 µmol) *rac*-**5** in 9 ml of DMSO to the mechanically stirred enzyme suspension. After 3 h stirring the reaction was terminated by addition of 100 ml of ethyl acetate and subsequent removal of the enzyme preparation by filtration (Büchner funnel). The biocatalyst was washed successively three times with 200 ml of ethyl acetate and three times with 300 ml of the buffer solution. The organic and aqueous solutions were combined and the aqueous layer was adjusted to pH < 3 with 6 *N* hydrochloric acid. The organic layer was separated and washed twice with ca. 200 ml of 6 *N* aqueous KOH solution to remove the DMSO, phenylacetic acid, and HCl. The organic extract was dried over Na_2SO_4 and the solvent evaporated; the solid crude product was purified by recrystallization from acetonitrile at −20 °C to yield 112 mg (50%, related to *rac*-**5**) of the unchanged substrate **5**. The acidic aqueous layer containing the hydrochloride of the biotransformation product was adjusted to pH 10 with 6 *N* aqueous KOH solution and then extracted with 800 ml of ethyl acetate. The organic layer was washed twice with ca. 200 ml of 6 *N* aqueous KOH solution to remove the DMSO and then dried over Na_2SO_4. After removal of the solvent *in vacuo* the crude product was purified by Kugelrohr distillation (80 °C/0.1 Torr) to give 54.3 mg (40%, related to *rac*-**5**) of (*R*)-**4** as a colourless

liquid which partly crystallized at room temperature to give a solid of m.p. 78°C. The spectroscopic properties of the product were identical with those of chemically prepared *rac*-**4** (see above).

^{1}H NMR spectroscopic studies and GLC analyses of the biotransformation product, after derivatization with (*S*)-MTPA (see above), revealed the (*R*)-configuration for the excess enantiomer of **4** and an enantiomeric purity of 92% ee.

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