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Biotransformations of organosilicon compounds: enantioselective reduction of acyl silanes by means of baker's yeast

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Abstract

The enantioselective reduction of acyl silanes has been performed employing baker's yeast (BY) in fermenting conditions: a series of substrates of different structure was investigated, showing that the reactivity as well as the level of enentioselectivity depends on the steric bulk of the substituents on the acyl silane. The products α-hydroxy silanes were obtained with chemical and optical yields over 90% in the most favourable cases.

Keywords: Bioreduction; Baker's yeast; Acyl silanes; α-Hydroxy silanes; Asymmetric synthesis

1. Introduction

In recent years, many investigations have been carried out in order to exploit biocatalysis (using either isolated enzymes or whole cell systems) for the preparation of chiral, not-racemic compounds [1,2].

Among the various possible biotransformations, microbial reductions have been studied as a tool to synthesize chiral alcohols from carbonyl compounds: in particular, baker's yeast (BY) (*Saccharomyces cerevisiae*) emerged as one of the most frequently employed microorganism in whole cell conditions due to its large bioavailability, easiness of treatment and mild reaction conditions to perform asymmetric reductions [3,4].

On the other hand, the interest in the use of unnatural or unconventional compounds as enzyme substrates is continuously growing in order to test the synthetic potential of biotransformations, as well as to investigate in detail the mechanism of enzymatic catalysis. In particular, the biotransformation of organosilanes [5–7] could lead to new results both in the production of useful organosilicon compounds in optically active form and in a deeper investigation of enzyme activity.

Acyl silanes constitute a particular class of functional organosilicon compounds [8,9]: they can be considered as synthetic equivalents of aldehydes provided with enhanced chemical stability; moreover, the presence of a bulky SiR_3 substituent can lead to higher stereodifferentiation in their reactions [10]. We have recently developed synthetic methods for obtaining acyl silanes of various structures and characterised by the presence of additional functional groups [11], giving us the opportunity to study their

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reactions and, in particular, their reduction to α-hydroxy silanes.

The enantioselective reduction of acyl silanes to α-hydroxy silanes has been the subject of investigations where both chiral, not-racemic chemical reagents [12–16] and biological agents have been used: in this latter case, the bioreduction was investigated employing the whole cell approach only. Syldatk et al. [17] indicated *Trigonopsis variabilis* and *Corynebacterium dioxidans* as the best biocatalysts in terms of activity and enantioselectivity for this reaction after screening of 30 strains of microorganisms (bacteria, fungi, green algae and yeasts) on a single substrate; later, the two selected microorganisms were tested with few more acyl silanes [18,19]. More recently, Bienz reported [20] the enantioselective reduction of different acyl silanes employing strains of *T. variabilis* as either free or immobilized resting cells, with high chemical and optical yield.

These findings point to an easy interaction between the acyl silanes and the oxido-reductases of the microorganisms tested, even though pronounced substrate inhibition was recognized [20]. Since the asymmetric reduction of carbonyl compounds by means of BY is one of the most widely used bioconversion, we choose to investigate this reaction employing a series of acyl silanes carrying different substituents with BY as biological reducing agent.

In this paper, the application of BY in fermenting conditions to the enantioselective reduction of acyl silanes **1a**–**j** is described, showing the effects that the substituents present either on silicon or on carbon may have in terms of the asymmetric induction observed.

2. Experimental

2.1. Apparatus and materials

Infrared spectra were obtained with a Perkin Elmer mod. 257 spectrometer. NMR spectra were recorded at 300 MHz (^{1}H) or 75.2 MHz (^{13}C) with a Varian Gemini 300 spectrometer using $CDCl_3$ as solvent if not otherwise indicated; ^{13}C multiplicities were assigned through DEPT experiments. Optical rotations were measured in the indicated solvents at room temperature employing a Perkin Elmer mod. 341 automatic polarimeter. Mass spectra were obtained on a VG 7070 E instrument in the E.I. ionization mode. Chromatographic separations were performed with E. Merck silica gel 60 (70–230 mesh); preparative layer chromatography was done with 20×20 plates coated with E. Merck silica gel 60 PF_{254}. Acyl silanes **1a**–**j** have been obtained according to published procedures [11,21]: characterisation is reported for new compounds, 6-(2,3-dihydroxypropoxy)-hexanoyl trimethyl silane **1h** and 3-hydroxy-4-phenyl butanoyl trimethylsilane **1i**, obtained according to the dithiane method (Corey–Seebach procedure [21]).

- 6-(2,3-Dihydroxypropoxy)hexanoyl trimethyl silane **1h** (94%): oil; I.R. (film): ν_{max} 3400 (OH), 1630 (COSi) cm^{-1}; ^{1}H NMR: δ 0.145 (9H, s, $SiMe_3$), 1.1–1.6 (6H, m, 3 CH_2), 2.55 (2H, t, CH_2), 3.25–3.90 (9H, m, $CH_2OH + CHOH + CH_2OCH_2$), ppm; ^{13}C NMR: δ 248.96 (CO), 72.00 (CH_2O), 71.25(CH_2O), 70.65 (CHO), 63.85 (CH_2O), 48.16 (CH_2), 29.25 (CH_2), 25.62 (CH_2), 21.63 (CH_2), −3.29 (3Me, $SiMe_3$) ppm; M.S: m/z 262 (M^+), 234 (M^+–28), 231 (M^+–29, 0.5%), 187, 171, 151, 149, 129, 101, 73 ($SiMe_3$; 100%), 69.
- 3-Hydroxy-4-phenyl butanoyl trimethylsilane **1i**, (86%) prepared according to the dithiane method modified as in Ref. [22]: oil; I.R. (CCl_4): ν_{max} 3550 (OH), 1640 (COSi) cm^{-1}; ^{1}H NMR: δ 0.20 (9H, s, $SiMe_3$), 2.60–2.85 (4H, m, $CH_2 + CH_2$), 3.1 (1H, br.s, OH), 4.25 (1H, m, CHOH), 7.15–7.35 (5H, m, ArH) ppm; ^{13}C NMR: δ 250.06 (CO), 137.97 (Cq), 129.22 (2CH), 128.26 (2CH), 126.28 (CH), 67.95 (CH), 53.30 (CH_2), 42.79 (CH_2), −3.60 (3Me, $SiMe_3$) ppm; MS: m/z 236 (M^+), 218 (M^+–H_2O) 217 (M^+–H_2O–H), 120 ($PhCH_2CHO$), 117 ($CH_3COHSiMe_3$), 91, 75, 73 ($SiMe_3$, 100%).

BY was purchased from Giuliani Pharmaceuticals as the formulation *Sillix* used as food supplement.

2.2. Methods

BY (*Sillix*) (5 g) is suspended in tap water (200 ml) and stirred at 35°C for about 30 min; once the cell growth is started, the suspension is transferred to a 2-l round bottomed flask, equipped with a mechanical stirrer and placed in a bath thermostatted at 31 ± 1°C: tap water (800 ml) and sucrose (13 g) are

added and the fermentation is monitored through the evolution of CO_2. After 30 min of constant gas evolution, acyl silane **1** (0.5 g) is added dissolved in 5 ml of ethanol; the conversion of the starting material could be followed either by TLC or GC-MS: when needed, further sucrose (5 g) was added. When the reaction was terminated, Hyflo SuperCel (Aldrich) (5 g) was added with stirring, then the reaction mixture was filtered on a large sintered glass-filtering funnel covered with additional Hyflo SuperCel (10 g). The aqueous phase is saturated with NaCl and extracted three times with ethyl acetate (3×500 ml); the solid pad is washed with ethanol, then with diethyl ether; the organic extracts are collected together, dried over $MgSO_4$ and evaporated to dryness at the rotavapor. The residue was analyzed routinely (GC-MS and ^{1}H NMR) and purified by column chromatography.

2.3. Analysis and characterisation of the products

Enantiomeric excesses of α − hydroxy silanes **2** were determined by one of the following methods: (a) measure of the optical purity by comparison with α values from the literature; (b) NMR analysis of the MTPA esters (Mosher's method) [23]; (c) NMR analysis in the presence of the chiral shift reagent Eu $(hfc)_3$; (d) HPLC analysis on a chiral Supelcosil-LC (R)-urea column, 25 cm × 4.6 mm, isocratic elution, mobile phase *n*-hexane/ethyl acetate/isopropanol; UV detection at the λ_{max} of the products.

2.3.1. Phenyl trimethylsilyl carbinol **2a**

Chromatography: petroleum ether/diethyl ether 10:1; oil; $[\alpha]_{589}$ −99.8° (C 1.01, $CHCl_3$). Enantiomeric excess (methods a and c): over 95%.

2.3.2. Phenyl (dimethyl phenyl silyl) carbinol **2b**

Chromatography: petroleum ether/diethyl ether 10:1; oil; $[\alpha]_{589}$ −58.1° (C 1.04, $CHCl_3$). Enantiomeric excess (method b): 42%.

2.3.3. Cyclohexyl trimethylsilyl carbinol **2d**

Column chromatography (petroleum ether/diethyl ether 20:1), then preparative plate chromatography (petroleum ether:diethyl ether 5:1); oil: ^{1}H NMR δ 0.04 (9H, s, $SiMe_3$), 1.05 ÷ 1.85 (11H, m, CH_2 + CH), 3.2 (1H, d, *J* 5.7 Hz, CHOH), 4.7 (1H, br.s., OH) ppm; ^{13}C: δ −2.47 (3Me, $SiMe_3$), 26.34 (CH_2), 26.37 (CH_2), 26.51 (CH_2), 29.40 (CH_2), 30.67 (CH_2), 42.22 (CH), 71.61 (CHOH) ppm; MS: *m/z* 186 (M^+), 171 (M^+–CH_3), 129, 112 (M^+–$HSiMe_3$), 81, 73 ($SiMe_3$). $[\alpha]_{589}$ −11.65° (C 0.51, CH_2Cl_2). Enantiomeric excess (method b): 15%.

2.3.4. 1-Trimethylsilyl 1-butanol **2f**

Chromatography: petroleum ether/diethyl ether 10:1; oil; $[\alpha]_{589}$ −4.4° (C 2.39, $CHCl_3$). Enantiomeric excess (method b): 60%.

2.3.5. 1-Trimethylsilyl-1,5 hexanediol **2g**

Chromatography: petroleum ether/diethyl ether from 8:2 to 0:1; oil: ^{1}H NMR δ 0.09 (9H, s, $SiMe_3$), 1.1 (3H, d, CH_3), 1.25 ÷ 1.7 (6H, m, 3 CH_2), 2.4–2.7 (2H, br.m, 2OH), 3.3 (1H, dd, *J* 9.8 and 4.4 Hz, CHOH), 3.7 (1H, m, CHOH) ppm; ^{13}C NMR (mixture of syn/anti-isomers, not fully separated, in a ratio about 1.5:1) δ −3.98 (3Me, $SiMe_3$), 22.68 and 22.77 (CH_2), 23.34 and 23.56 (Me), 32.70 and 33.21 (CH_2), 38.49 and 38.87 (CH_2), 65.15 and 65.65 (CHOH), 67.42 and 67.77 (CHOH) ppm; MS: *m/z* 190 (M^+, less than 1%), 189 (M^+–1, 1%), 175 (M^+–15, 0.6%), 172 (M^+–18, 0.8%), 157 (M^+–18–15, 11%), 143 (6%), 129 (36%), 101 (20%), 73 ($SiMe_3$, 100%); $[\alpha]_{589}$ −5.20°, $[\alpha]_{546}$ −6.13° (C 4.39, $CHCl_3$). Enantiomeric excess (method d): 35 ± 5%.

2.3.6. 6-(2,3-Dihydroxypropoxy)-1-trimethylsilyl-1-hexanol **2h**

Chromatography: diethyl ether:ethanol 2:1; oil; ^{1}H NMR δ −0.02 (9H, s, $SiMe_3$), 1.2–1.7 (8H, m, $4CH_2$), 3.0–3.4 (3H, br. 3OH), 3.2–3.9 (8H, m, CH_2O + CHO) ppm; ^{13}C NMR δ −3.99 (3Me, $SiMe_3$), 25.90 (CH_2), 26.40 (CH_2), 29.30 (CH_2), 33.17 (CH_2), 64.03 (CH_2O), 65.77(CHO), 70.58 (CHO), 71.54 (CH_2O), 72.26 (CH_2O) ppm; MS: *m/z* 191 (M^+–$SiMe_3$), 173 (M^+–$SiMe_3$–H_2O), 157 (M^+–$SiMe_3$–H_2O–O, 22%), 129 (56%), 101 (12%), 73 ($SiMe_3$; 100%); IR (liquid) ν_{max}: 3600–3100 (–OH); 2940–2820 (CH); 1240 ($SiMe_3$) cm^{-1}.

$[\alpha]_{589}$ +6.7°, $[\alpha]_{546}$ +7.5° (C 1.25, $CHCl_3$). Enantiomeric excess (method d): 43 ± 5 %.

*2.3.7. 1-Trimethysilyl 4-phenyl 1,3-butandiol **2i***

First test: weight ratio BY:substrate 40.6:1. Chromatography: petroleum ether:diethyl ether; solid, mixture of syn/anti-isomers in a ratio 4:1, m.p. 84–87°C (diethyl ether); ^{1}H NMR (CD_3OD) δ (syn-isomer) 0.10 (s, 9H, $SiMe_3$); 1.8–1.9 (2H, m, O–C–CH_2C–O), 2.8–3.1 (2H, dq, CH_2Ph), 3.65 (1H, dd, *J* 10.0 and 4.5 Hz, CH(OH)Si), 4.3 (1H, m, CH(OH)CH_2Ph), 4.9 (2H, br.s., 2OH), 7.3 ÷ 7.6 (5H, m, Ph); (anti-isomer) 0.15 (9H, s, $SiMe_3$), 1.6 ÷ 1.8 (2H, m, O–C–CH_2–C–O); 2.9 (2H, dq, CH_2Ph); 3.80 (1H, dd, *J* 11.7 and 2.1 Hz, CH(OH)Si), 4.25 (1H, m, CH(OH)CH_2Ph), 5.1 (2H, br.s, 2OH), 7.3 ÷ 7.5 (5H, m, Ph) ppm; ^{13}C NMR (CD_3OD) δ (syn-isomer): −3.68 (3Me, $SiMe_3$), 40.35 (CH_2), 45.0 (CH_2), 66.2 (CHOH), 75.09 (CHOH); (anti-isomer): −3.58 (3Me, $SiMe_3$), 40.89 (CH_2); 45.90 (CH_2), 62.61 (CHOH), 70.66 (CHOH); (syn + anti-isomers): 127.36 (CH), 129.52 (2CH), 130.82 (2CH), 130.91 (CH), 140.85 (Cq) ppm; MS: *m/z* 220 (M^+–H_2O), 205 (M^+–H_2O–Me), 147 (M^+–CH_2Ph), 129, 91 ($C_7H_7^+$), 73 ($SiMe_3^+$). IR (CCl_4) ν_{max}: 3600–3200 (–OH) cm^{-1}. $[\alpha]_{589}$ +0.89° (C 1.46, MeOH).

Second test: weight ratio BY:substrate 9.7:1. $[\alpha]_{589}$ +2.5° (C 2.59, MeOH), $[\alpha]_{589}$ +2.1° (C 1.27, Dioxane).

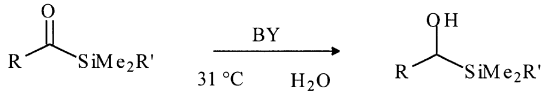
*2.3.8. Methyl 3-(dimethylphenyl)silyl-3-hydroxypropanoate **2j***

Chromatography: petroleum ether/diethyl ether from 50:1 to 2:1; oil: ^{1}H NMR δ 0.30 (6H, s, $SiMe_2$), 2.25 (1H, br.s., OH), 2.3–2.5 (2H, m, CH_2), 3.60 (3H, s, OMe), 3.90 (1H, dd, *J* 3.25 and 11 Hz, CH(OH)), 7.30–7.55 (5H, m, ArH) ppm; ^{13}C NMR δ −5.98 and −5.62 (2Me, $SiMe_2$), 37.22 (CH_2), 51.71 (MeO), 61.12 (CHOH), 127.93 (2 CH), 129.50 (CH), 134.05 (2 CH), 135.9 (Cq), 174.17 (COO) ppm; MS: *m/z* 221 (M^+–17), 220 (M^+–18), 219 (M^+–18–1), 205, 193, 163, 159, 137, 135 ($SiMe_2$Ph), 105 (SiPh). IR (liquid film) ν_{max} 3500 (OH), 1735 (COO) and 1250 (SiMe) cm^{-1}. $[\alpha]_{589}$ −4.44°, $[\alpha]_{546}$ −5.44° (C 3.69, $CHCl_3$). Enantiomeric excess (method c): 30 ± 5%.

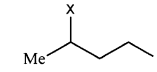
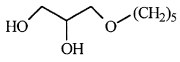
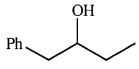
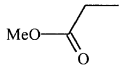
3. Results and discussion

The biotransformation of a series of acyl silanes in the presence of fermenting BY is presented in Scheme 1: α-hydroxy silanes **2a**–**j** are obtained; the yields in isolated products and the enantioselectivities observed are summarized in Table 1. Acyl silanes **1a**–**c** are characterised by the presence of an aromatic substituent directly bonded to the carbonyl, whereas one of the Si substituent can be either Me (**1a**) or Ph (**1b**). The trimethylsilyl derivative **1a** is more reactive with BY affording the optically active α-silylbenzyl alcohol in good yield: the conversion of **1a** is almost complete in a few hours and the optical purity of isolated **2a** is around 100% (entry 1, Table 1). Compared with **1a**, the dimethylphenyl silyl derivative show interesting differences: reactivity is much lower (conversion around 75% after 3 days) and, significantly, the e.e. of the product **2b** is drastically reduced (entry 2). Even less reactive is the *p*-fluorophenyl derivative **1c**, which could be recovered almost quantitatively after 9 days (entry 3). Optical rotations of hydroxy silanes **2a** and **2b** are both negative at 589 nm: this allows us to assign the (*S*) absolute configuration to **2a** and **2b**, based on the detailed study done by Biernbaum and Mosher [24].

The reduction of acyl silanes carrying cycloalifatic and alifatic saturated groups **1d**–**f** was subsequently tested (Table 1, entries 4–6): in this case also, one of the Si substituent can be either Me or Ph. The reactivity of the linear derivative **1f** is very similar to that of **1a**, but with reduced enantioselectivity (entry 6); acyl silane **1d**, that carries a bulkier cyclic residue, show a very reduced reactivity, coupled with a low value of e.e. (entry 4). Finally, substrate **1e** characterised by sterically demanding substituents both on carbon and on silicon, becomes unreactive (entry 5). Again, products **2d** and **2f** are levorotatory: this corresponds to an (*S*) absolute configuration for **2d**, which is known [15], and could reasonably suggest the same configuration for **2f** as well. Since products **2a**–**b** were obtained in the (*S*) configuration also, this implies that the reduction has occurred by stereoselective transfer of hydride to the Re face of the corresponding acyl silanes. This preference is in agreement with the so-called Prelog rule [25], which is often obeyed in the reduction of



1a -j 2a -j

R	R'	1	2
Ph	Me	**1a**	**2a**
Ph	Ph	**1b**	**2b**
p-F-C_6H_4-	Ph	**1c**	----
cycloHexyl	Me	**1d**	**2d**
cycloHexyl	Ph	**1e**	----
n-C_3H_7	Me	**1f**	**2f**
	Me	**1g**	**2g**
	Me	**1h**	**2h**
	Me	**1i**	**2i**
	Ph	**1j**	**2j**

Scheme 1.

carbonyl compounds with BY; however, the opposite preference was found when cell cultures other than BY were used, affording α-hydroxy silanes of (*R*) configuration by bioreducytion of acyl silanes [20].

Table 1
Enantioselective reduction of acyl silanes **1a**–**j** by BY

Entry	Acyl silane **1**	Time	Recovered **1** (%)	Yield **2**[a]	e.e. **2**
1	**1a**	20 h	5	**2a** 65%	> 95%
2	**1b**	3 days	27	**2b** 86%	42%
3	**1c**	9 days	90	**2c** traces	–
4	**1d**	5 days	75	**2d** 44%	15%
5	**1e**	3 days	100	–	–
6	**1f**	18 h	0	**2f** 70%	60%
7	**1g**	2 days	30	**2g** 54%	35%
8	**1h**	18 h	0	**2h** 65%	43%
9	**1i**[b]	4.5 h	0	**2i** 83%	n.a.[c]
10	**1i**[d]	6 h	0	**2i** > 95%	n.a.[c]
11	**1j**	20 h	> 10	**2j** 35%	30%

[a] Conversion yields are based on reacted **1**.
[b] Weight ratio BY:substrate 40.6:1.
[c] n.a.: not available.
[d] Weight ratio BY:substrate 9.8:1.

These findings about structure/reactivity relationship are in line with the previous generalizations reported for the reduction of carbonyl compounds by BY, which suffers steric inhibition. It is known that sterically hindered ketones (*t*-butyl methyl ketone, 4-octanone, *i*-butyl *i*-propyl ketone, *n*-amyl-phenyl ketone) are not reduced by BY [26]; on the other hand, it should be considered that the $SiMe_3$ substituent is sterically less demanding than the constitutionally similar *t*-Bu group, due to the longer C—Si bond distance: for these reasons, it is conceivable that trimethylsilyl acyl silanes have a reactivity similar to that of unhindered ketones; in those compounds, it is well-known that the presence of other polar functional groups in the molecule allows a better interaction of the carbonyl compound with the enzymes dehydrogenases present in the yeast, leading to an enhancement of reactivity. The same effect

could have been present for acyl silanes: hence, the biotransformations of derivatives **1g**–**j**, containing additional functionalities, were investigated.

Since it was evident from the previous results that acyl silanes carrying a phenyl group on silicon show a lower reactivity, we choose to prepare new trimethylsilyl acyl silanes containing polar groups following the Corey–Seebach approach, where 2-trimethylsilyl 1,3-dithiane is alkylated and the carbonyl group subsequently liberated through hydrolysis: in this way, dialkyl halogenides or other polyfunctionalised halogenides can be introduced. Alternatively, the reaction of 2-silyl 2-lithio dithianes with epoxides leads, after deblocking, to β-hydroxyacyl silanes, which can be further transformed [22]. These concepts have been applied to the synthesis of **1h** and **1i** (see Experimental); in fact, the newly prepared compound **1i** with hydroxy groups in β position showed a marked increase in reactivity (entries 9, 10), whereas the derivatives **1g** and **1h**, carrying either a bromine in δ- or a dihydroxylated residue connected through an ether group in position 5, displayed a reactivity not very different from **1f** (entries 7, 8). Acyl silane **1g** (X = Br) afforded, on interaction with BY, the diol **2g** (X = OH) where the substitution of the bromine on the secondary carbon with the OH group has occurred together with the reduction of the carbonyl; it is known indeed that hydrolases are present and active in BY [4]. In the case of **1i**, it is possible to demonstrate that this substrate has a reduced inhibition effect on the BY reductases, because its rate of conversion is not influenced by a fivefold variation in the substrate/BY ratio (entries 9 vs. 10). The product is the diol **2i**, which is formed as a mixture of syn/anti-stereoisomers (syn-isomer favoured in a ratio 4:1). Since all the hydroxy silanes **2** were prepared also in racemic form through chemical reduction of the corresponding acyl silanes, employing either $LiAlH_4$ or $NaBH_4$, in order to obtain the model compounds, we could observe in the case of the reduction of **1i** a striking difference in the stereoselectivity of the biological process with respect to the chemical one: on using $LiAlH_4$, the stereisomeric ratio found for **2i** is syn-diol/anti-diol 1:3. The formation of two inseparable stereoisomers in the bioreduction of **1i** hampers the determination of the e.e, but the quite low values of optical activity found for **2i** presumably indicates similar low values of e.e.s. It is worth noting that the increase in substrate/BY ratio causes a sizeable rise in the rotatory power of **2i** (see Experimental), whereas the chemical yield is almost unaffected. It has been already pointed out [27] that the enantioselectivity for BY reduction can be a function of substrate concentration, due to the presence of different enzymes oxidoreductase with opposite stereospecificities and different affinities for the substrate. A reasonable assumption is that the low enantioselectivities observed in the reduction of the acyl silanes carrying extra functionalities (like **1g**–**j**) is depending on a higher, hence, less selective affinity for more BY reductases of opposite enantiospecificities. This hypothesis could be supported by the reduction of **1j**: this acyl silane can be considered the analog of β-ketoesters, which are the substrates most frequently employed in BY reductions [4]. Our results are in line with the hypotheses already proposed. The reactivity of **1j** (entry 11) is intermediate in comparison with that of **1f** and **1b** (entries 6, 2) probably due to the steric effect of the Ph group bonded to Si, whose retarding effect could be counterbalanced by the presence of the polar COOMe group; the enantioselectivity is low (30%), and this is in line with the operation of more enzyme reductases with opposite stereochemical bias.

Some observations that can be drawn from the preliminary results presented are: BY in fermenting conditions can be used for the enantioselective reduction of acyl silanes; a quite large variety of structures are accepted, with a preference for substrates containing either an aromatic or a polar group; the reduction suffers steric inhibition, though acyl silanes are more reactive than ketones of similar structure; α-hydroxy silanes are obtained in optical yields from medium to high.

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