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Reduction of Carbonyl Compounds by Using Polymethylhydrosiloxane: Reactivity and Selectivity

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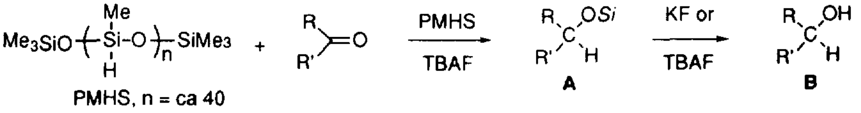
Abstract: Reduction of aldehydes and ketones with PMHS [Me_3SiO-$(SiMe(H)O)_n$-$SiMe_3$] proceeded smoothly in the presence of Bu_4NF at -70 °C or 0 °C within 60 min in THF. High stereo- and chemoselectivities as well as functional group tolerance of this system are also presented. © 1997, Elsevier Science Ltd. All rights reserved.

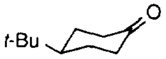
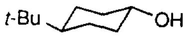
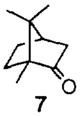
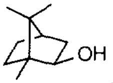
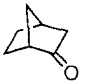
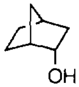
INTRODUCTION

Since neutral organosilanes themselves are poor compounds for reduction of carbonyl compounds to alcohols, activating agents with the proper choice of solvents have been investigated extensively.[1] Much attention has been paid to generate active species. However selectivities of several kinds, another important aspect in organic synthesis, are not yet examined in detail except for one report studying stereoselection for acyclic ketones.[1e,f] Among organosilanes studied thus far, polymethylhydrosiloxane (PMHS) is an attractive reagent for reduction of carbonyl compounds in terms of its low price, stability against air and moisture, and easy handling.[2,3] In addition, steric effect is expected from its polymeric structure. In the early stage of investigation PMHS has been used to prepare tin hydrides from organotin oxides.[4] Then inorganic fluorides and HCOOK in DMF or DMSO have been published to be effective for the reduction, where pentacoordinate hydridosilicates are postulated as active species.[5] Recently titanocenes have been shown to be a catalyst for ester reduction[6] where Cp_2Ti-H is active species and these results led to asymmetric reduction of ketones by using chiral titanocenes.[7] Among these methods of activation, the second one seems to be attractive because bulky PMHS as such are involved in the reduction as pentacoordinate hydridosilicate and thence high stereoselection is expected. However, the published conditions limit further investigation due to the low reactivity especially toward ketones under the conditions using excess activating agents in the non-volatile polar solvent, and thence stereoselectivity is scarcely reported: the only example is reduction of 4-*tert*-butylcyclohexanone **(1)** using excess KF in DMF to produce a mixture of *trans* and *cis* 4-*tert*-butylcyclohexan-1-ol **(2)** with rather low *trans* : *cis* selectivity of 82 : 18.[5a] We considered that a soluble fluoride anion would be powerful



(1)

Table 1. Reduction of Cyclic Ketones with PMHS and TBAF.[a]

run	substrate	TBAF[b] equiv	temp. (°C)	time (min)	yield[c] (%)	major product	ratio[d] *trans* : *cis*
1	 **1**	0.05	-70	30	86 (95)[e]	 *trans*-**2**	96 : 4
2	**1**	1	-70	30	quant.	*trans*-**2**	96 : 4
3	**1**	0.05	0-5	5	quant.	*trans*-**2**	87 : 13
4	 **3**	0.05	-70	30	quant.	 *trans*-**4**	91 : 9
5	 **5**	0.05	-70	60	89	 *trans*-**6**	73 : 27
6	 **7**	0.05	-70	60	85	 *exo*-**8**	96 : 4
7	 **9**	0.05	-70	40	82	 *endo*-**10**	>99 : 1

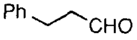
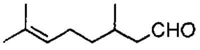
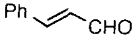
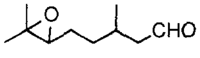
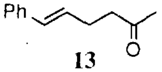
[a] Reactions were carried out with ketones (2 mmol), PMHS (1.3-1.5 mol equiv of hydrogen atom), and TBAF (0.05 or 1 equiv). [b] When 0.05 equiv of TBAF was used, the initially formed silyl ethers were hydrolyzed with TBAF (1 equiv) in THF unless otherwise noted. [c] Isolated yields. [d] Determined by ^{1}H NMR (300 MHz). [e] Isolated yield after desilylation of the silyl ether intermediate by KF (5 equiv) in a 1 : 1 mixture of Et_2O and acetone.

activating agent of PMHS based on the observation reported.[1c] Herein we report that Bu_4NF (TBAF) is a highly effective catalyst for reduction of aldehydes and ketones to alcohols **B** (eq 1) and that high stereoselectivity is observed in the reduction of cyclic ketones. Chemo- and functional group-selectivities are also presented.

RESULTS AND DISCUSSION

Initially, reaction conditions were explored with 4-*tert*-butylcyclohexanone (**1**) using PMHS (1.3-1.5 mol equiv of hydrogen atom, n = ca 40) and TBAF (5 mol % or 1 equiv) in THF.[8] Results are summarized in Table 1. When 5 mol % of TBAF was added to a solution of **1** and PMHS in THF at -70 °C immediate evolution of a gas was observed.[9] After 30 min production of the silyl ether of type **A** was confirmed by TLC and ^{1}H NMR (300 MHz) and subsequent treatment with TBAF (1 equiv) afforded 4-*tert*-butylcyclohexan-1-

Table 2. Reduction of Carbonyl Compounds with PMHS-TBAF.[a]

run	substrate	temp. (°C)	yield (%) of alcohol[b]	run	substrate	temp. (°C)	yield (%) of alcohol[b]
1	 **11**	0-5	85[c]	5	 **14**	-70	96[c]
2	 **12**	-70	90-100[d]	6	**14**	0-5	83[c]
3	**12**	0-5	quant.[d]	7[e]	 **15**	0-5	98
4	 **13**	-70	89	8	MeOOC-$(CH_2)_4$-CHO **16**	-70	quant.

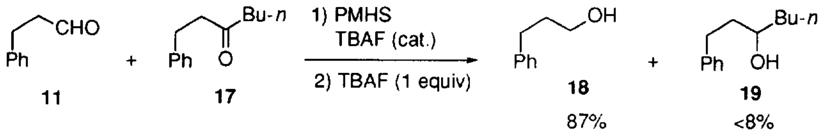
[a] All the reductions were carried out with PMHS (1.3 - 1.5 mol equiv) and TBAF (5 mol %) in THF at -70 °C or 0 °C for 10-15 min and the silyl ethers were decomposed by addition of TBAF (1 equiv) unless otherwise noted. [b] Isolated yields. [c] The silyl ether was hydrolyzed to the alcohol by addition of KF (5-10 equiv) in acetone/Et_2O (1 : 1) at room temperature for 1-4 h. [d] Major product was cinnamyl alcohol and 1-5% of saturated alcohol was co-produced. [e] The reaction was carried out in the presence of 1 equiv of TBAF.

ol (**2**) in 86% yield (run 1) after usual work-up. Addition of excess KF in a mixed solvent of Et_2O and acetone (1 : 1) was found to be also effective for liberation of free alcohol **2** from the silyl ether intermediate (footnote *e* of run 1). The later non-aqueous work-up is much simpler than the former. Ratio of *trans* : *cis* isomer of **2** thus obtained was 96 : 4 by ^1H NMR (300 MHz). Reaction in the presence of 1 equiv of TBAF was operationally more convenient to afford **2** directly with the same isomeric ratio (run 2). However, reaction at 0-5 °C resulted in an inferior stereoselection of 87 : 13 (run 3). It is noteworthy that the present ratio is higher than previously reported one using PMHS activated by KF (*vide supra*).[5a,10] The selectivity is also higher than those obtained with bis(diolato)hydridosilicates derived from Cl_3SiH and catechol or 2,2'-dihydroxybiphenyl anion (56 : 44 or 33 : 67)[1h] and with $LiAlH_4$ (94 : 6).[11,12] From synthetic point of view, the major *trans* isomer is of product development control[13] and the present system is complementary with *cis* selective reagents such as L-Selectride®.[14]

Reduction of the cyclic substrates **3**,**5**,**7**, and **9** was examined under the best conditions for **1** (Table 1, run 1). Results are also summarized in Table 1. All the ketones were reduced within 60 min into the corresponding alcohols **4**,**6**,**8**, and **10** in good yields. As in the case of **1**, the ketone **3** afforded stereoselectively the *trans* stereoisomer **4** of product development control (run 4). The selectivity was higher than that recorded with $LiAlH_4$ (81 : 19).[12a] However, observed selectivity for **5** was lower than the formers (run 5). For ketones of the camphor type, the major stereoisomers **8** and **10** were those produced by the "hydride" attack from the less hindered sides of **7** and **9**, respectively (runs 6 and 7).

We next turned our attention to the compatibility of the functional groups. Substrates examined and yields of the alcohols produced are shown in Table 2. All the reductions were completed within 15 min at -70 and/or 0 °C with high yields. Olefins of several kinds, epoxide, and ester were not reduced at all. Reduction of **11** was also carried out in the presence of 1 equiv of 11-bromo-1-undecene at 0-5 °C. Only **11** was participated in the reaction, and the alcohol from **11** was obtained in high yield and the bromide was recovered.

Finally chemoselectivity of the reduction was examined briefly. Thus, competitive reduction of **11** and **17** (1 : 1) was carried out with PMHS (1.1 equiv) and TBAF (0.05 equiv) at -70 °C for 20 min and the silyl ether intermediates were hydrolyzed with TBAF (1 equiv) (eq 2). ^{1}H NMR (300 MHz) of the crude products revealed formation of **18** and **19** in a ratio of >11 : 1 and chromatographic purification afforded **18** in 87% yield.



11 + **17** → **18** 87% + **19** <8% (2)

According to the mechanism for reduction of carbonyl compounds with hydrosilanes catalyzed by fluoride anion,[1e-g, i,j,15] the present reduction seems to follow the cycle illustrated in Fig. 1. Fluoride anion in THF attacks the silicon atom of PMHS to generate reactive pentacoordinate hydridosilicates C or THF-coordinated hexavalent silicates, which deliver the hydride to the carbonyl carbon to afford the intermediates D, and production of fluoride anion and the silyl ethers A closes the cycle. Steric interaction of the carbonyl compounds and bulky polymeric species C are apparently responsible for the observed high stereoselection.

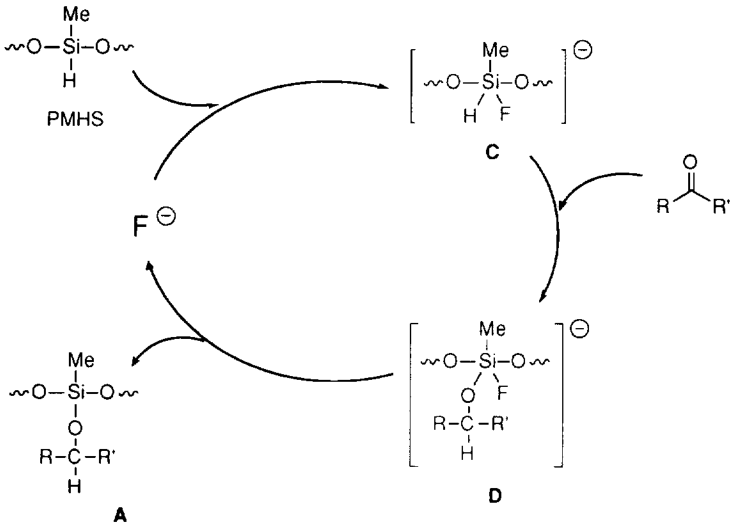


Fig. 1

CONCLUSION

We presented reduction of carbonyl compounds by using chemically inert and thence easily handling PMHS, which could be switched to the active species when required by addition of a catalytic amount of TBAF. Reduction went to completion even at -70 °C within 1 h for ketones and aldehydes, the latter being reduced chemoselectively. Esters, epoxides, olefins, and bromides were found to be compatible with PMHS/TBAF system. For substituted cyclohexanones, the alcohols of product development control were the major stereoisomers with higher stereoselection than that obtained with $LiAlH_4$, which is known to be the best reagent for production of such stereoisomers. In addition, the observed selectivity is opposite to that obtained with *cis* selective reagents such as Selectrides®. THF was a sufficient solvent for the reduction: non-volatile polar solvents such as HMPA, DMF, DMSO are not necessary at all. Thus, the present reduction is now a choice of large scale and selective transformation of such carbonyl compounds to the alcohols.

EXPERIMENTAL

General: Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Polymethylhydrosiloxane (PMHS, n = ca 40) and 1 M solution of Bu_4NF (TBAF) in THF were purchased from Aldrich. Most of carbonyl compounds obtained from companies were used without further purification except for **13**, **15**, and **16**. Preparation of the ketone **13** was given below and the aldehydes **15** and **16** were prepared according to the literature procedures.[16,17] Mixtures of *trans* and *cis* isomers presented in Table 1 were prepared according to the literature procedures[12,18] and their ^1H NMR (300 MHz) spectra were used as the references to determine the ratios of the alcohols produced by PMHS reduction. The diagnostic signals are listed in Table 3.

(*E*)-6-Phenyl-5-hexen-2-one (13). To a suspension of NaH (363 mg, 50% dispersion in oil, 7.56 mmol) in THF (15 mL) was added *tert*-butyl acetoacetate (1.03 g, 6.51 mmol) dropwise at 0 °C. After 30 min at 0 °C *n*-BuLi (3.1 mL, 2.1 M in hexane, 6.5 mmol) was added. The resulting mixture was stirred at the same temperature for 2 h and then poured into a mixture of AcOEt and aqueous 1 N HCl. The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to give crude *tert*-butyl 3-oxo-7-phenyl-6-heptenoate as an oil.

To a flask containing the crude product obtained above was added benzene (15 mL) and aqueous 1 N H_2SO_4 (1 mL) and the mixture was stirred under reflux for 4 days and diluted with brine. The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined extracts were washed with sat. $NaHCO_3$, dried over $MgSO_4$, and concentrated in vacuo to give an oil, which was purified by chromatography on silica gel to give (*E*)-6-phenyl-5-hexen-2-one (**13**) (792 mg, 90%), whose ^1H NMR spectrum was identical with that reported:[19] bp. 170 °C/ 3 mmHg (lit.[19] 100-102 °C/ 0.6 mmHg).

Typical procedure for the reduction including TBAF-workup: Preparation of 4-*tert*-butylcyclohexan-1-ol (2). To a solution of 4-*tert*-butylcyclohexanone (**1**) (308 mg, 2.0 mmol) and PMHS (180 mg, 1.5 mol equiv of hydrogen atom) in THF (4 mL) was added TBAF (0.1 mL, 1 M in THF, 0.1 mmol) at -70 °C. A gas evolved immediately.[9] After 30 min at -70 °C TBAF (2 mL, 1 M in THF, 2 mmol) was added to the solution. The resulting solution was warmed up to room temperature over 1 h and then poured into a mixture of Et_2O and brine. The mixture was made acidic (pH ca 2) by addition of aqueous 1 N HCl solution. The ethereal phase was separated, washed with sat. $NaHCO_3$, dried over $MgSO_4$, and concentrated in vacuo to give a solid, which was purified by chromatography on silica gel to afford 4-*tert*-butylcyclohexanol (**2**) (269 mg, 86%). The *trans* : *cis* ratio of **2** was 96 : 4 by ^1H NMR spectroscopy: mp 70-73 °C (lit.[12a] 82.5-83.5 °C for pure *trans* isomer) after sublimation (88-92 °C/ 4 mmHg).

Typical procedure for the reduction including KF-workup: Preparation of citronellol. To a solution of citronellal (**14**) (3.83 g, 24.8 mmol) and TBAF (1.2 mL, 1 M in THF, 1.2 mmol) in THF (50 mL) was added PMHS (1.93 g, 1.3 mol equiv of hydrogen atom) dropwise at 0 °C. After 10 min the solvent was removed in vacuo. The residue was dissolved in Et_2O (15 mL) and acetone (15 mL), and then KF (7.21 g, 124 mmol) was added to the solution. The resulting mixture was stirred vigorously for 4 h at room temperature and filtered through a pad of Celite® with Et_2O. The filtrate was concentrated to give the residue, which was distilled under reduced pressure to afford citronellol (3.20 g, 83%): bp ca 140 °C/ 5 mmHg; lit.[20] 108.4 °C/ 10 mmHg.

4-Methylcyclohexan-1-ol (4). Reduction of 4-methylcyclohexanone (**3**) (224 mg, 2.0 mmol) was

Table 3. Diagnostic Signals[a] in the ^{1}H NMR Spectra for the *trans* and *cis* Isomers.[b]

alcohol	chemical shift ppm	splitting pattern	coupling constant Hz
trans-**2**	3.51	tt,	J = 4.4, 10.8
cis-**2**	4.03	quintet,	J = 2.6
trans-**4**	3.53	tt,	J = 4.5, 11.1
cis-**4**	3.93	m	--
trans-**6**	3.11	dt,	J = 4.3, 9.6
cis-**6**	3.77	quintet,	J = 2.6
exo-**8**	3.61	dd,	J = 4.3, 6.8
endo-**8**	4.00	d,	J = 10
exo-**10**	3.74	d,	J = 6.8
endo-**10**	4.21	m	--

[a] The signals are for hydrogen attached to the carbon bearing hydroxyl group. [b] Measured in $CDCl_3$ using 300 MHz NMR.

carried out with PMHS (181 mg) and TBAF (0.1 mL, 0.1 mmol) in THF (4 mL) at -70 °C for 30 min to give **4** (226 mg, 100%, *trans/cis* = 91/9) after TBAF-workup: bp 96-101 °C/ 65 mmHg (lit.[4a] 55 °C/ 20 mmHg).

2-Methylcyclohexan-1-ol (6). Reduction of 2-methylcyclohexanone (**5**) (224 mg, 2.0 mmol) was carried out with PMHS (181 mg) and TBAF (0.1 mL, 0.1 mmol) in THF (4 mL) at -70 °C for 60 min to give **6** (204 mg, 89%, *trans/cis* = 73/27) after TBAF-workup.

Isoborneol (8). Reduction of camphor (**7**) (305 mg, 2.0 mmol) was carried out with PMHS (181 mg) and TBAF (0.1 mL, 0.1 mmol) in THF (4 mL) at -70 °C for 60 min to give **8** (263 mg, 85%, *endo/exo* = 4/96) after TBAF-workup: mp. 204-207 °C (lit.[20] 212 °C for pure *exo* isomer) after sublimation.

Norborneol (10). Reduction of norcamphor (**9**) (220 mg, 2.0 mmol) was carried out with PMHS (181 mg) and TBAF (0.1 mL, 0.1 mmol) in THF (4 mL) at -70 °C for 40 min to give **10** (183 mg, 82%, *endo/exo* = >99/1) after TBAF-workup: mp. 147-149 °C (lit.[21] 149-150 °C) after sublimation.

3-Phenyl-1-propanol. Reduction of 3-phenylpropanal (**11**) (247 mg, 1.84 mmol) was carried out with PMHS (211 mg) and TBAF (0.09 mL, 0.09 mmol) in THF (4 mL) at 5 °C for 10 min to give 3-phenyl-1-propanol (213 mg, 85%) after KF-workup.

3-Phenyl-2-propen-1-ol. Reduction of 3-phenylpropenal (**12**) (264 mg, 2.0 mmol) was carried out with PMHS (181 mg) and TBAF (0.1 mL, 0.1 mmol) in THF (4 mL) at -70 °C for 10 min to give 3-phenyl-2-propen-1-ol (268 mg, 100%) after TBAF-workup.

(*E*)-6-Phenyl-5-hexen-2-ol. Reduction of (*E*)-6-phenyl-5-hexen-2-one (**13**) (509 mg, 2.92 mmol) was carried out with PMHS (272 mg) and TBAF (0.15 mL, 0.15 mmol) in THF (7 mL) at -70 °C for 15 min to give (*E*)-6-phenyl-5-hexen-2-ol (458 mg, 89%) after TBAF-workup, whose ^{1}H NMR was identical with that reported.[22]

3,7-Dimethyl-6,7-epoxyoctan-1-ol. Reduction of 3,7-dimethyl-6-octen-1-ol (**15**) (105 mg, 0.618 mmol) was carried out with PMHS (55 mg) and TBAF (0.62 mL, 0.62 mmol) in THF (3 mL) at 5 °C for 15 min to give 3,7-dimethyl-6,7-epoxyoctan-1-ol (104 mg, 98%) after TBAF-workup, whose ^{1}H NMR spectrum was identical with that reported.[23]

Methyl 6-Hydroxyhexanoate. Reduction of methyl 6-oxohexanoate (**16**) (91 mg, 0.63 mmol) was carried out with PMHS (60 mg) and TBAF (0.03 mL, 0.03 mmol) in THF (2.5 mL) at -70 °C for 10 min to give methyl 6-hydroxyhexanoate (92 mg, 100%) after TBAF-workup, whose ^{1}H NMR was identical with that reported.[24]

Competitive reduction of 3-phenylpropanal (11) and 1-phenylheptan-3-one (17). To a solution of **11** (268 mg, 2.0 mmol), **17** (380 mg, 2.0 mmol), and PMHS (132 mg, 2.2 mmol of hydrogen atom) in THF (6 mL) was added TBAF (0.1 mL, 1 M in THF, 0.1 mmol) at -74 °C. A gas evolved immediately as mentioned above. After 20 min at -72 °C TBAF (2.0 mL, 1 M in THF, 2.0 mmol) was added to the solution. The resulting solution was warmed to room temperature over 1 h and the products were isolated as described above. Ratio of 3-phenyl-1-propanol (**18**) over 1-phenyl-3-heptanol (**19**) was determined to be >11 : 1 by ^{1}H NMR spectrum of the crude products. Purification by chromatography on silica gel afforded **18** (237 mg, 87%).

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8. Other solvents such as Et_2O, CH_2Cl_2 were not efficient.
9. The gas is conceivable to be hydrogen generated by reaction of the highly reactive pentacoordinate hydridosilicate and H_2O which could not be eliminated from the reaction flask: Cf. Corriu, R. J. P.; Guerin, C.; Henner, B. J. L.; Wang, Q. *Organometal.* **1991**, *10*, 3200-3205.
10. According to the referee a reduction of the ketone **1** by using 1,1,3,3-tetramethyldisiloxane was examined

under the identical conditions to give similar results (89% yield, *trans* : *cis* = 97 : 3). However, the reagent is 6 fold more expensive than PMHS based on the hydride involved.

11. To make an accuracy comparison, reduction with $LiAlH_4$ was carried out under otherwise identical conditions. The published ratios are ca 90 : 10, see ref 12.
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