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Journal of Organometallic Chemistry 624 (2001) 223–228

Journal of Organometallic Chemistry

www.elsevier.nl/locate/jorganchem

Stereoselective addition of organomanganese reagents to chiral acylsilanes and aldehydes

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Received 16 October 2000; accepted 22 November 2000

Abstract

Organomanganese halides and organomanganates prepared by transmetalation of organolithium and Grignard reagents add smoothly to the carbonyl moiety of acylsilanes and of substituted aldehydes bearing a chiral center at the α-position affording the desired alcohols in good to excellent yields and with essentially no undesired products from enolization. Comparison of the stereochemical outcome with that observed for other organometallic species, outlines the capability of organomanganese reagents to induce uniformly good diastereoselectivities, in a number of cases significantly higher than reported previously for these reactions. The key role displayed by the R_3Si group in promoting high 1,2-asymmetric induction, clearly emerges in the comparison of acylsilane **12** with the corresponding aldehyde **13**. The sense of the Cram/anti-Cram selectivity depends upon the nature of the carbonyl reagents engaged in these reactions.

Keywords: Organomanganese; Addition; Acylsilanes; Asymmetric induction

1. Introduction

Organometallic compounds and metal-mediated transformations are among the most powerful tools in synthetic organic chemistry [1]. Addition of organometallic compounds to aldehydes and ketones has been extensively studied. Starting from classical carbanions in the form of organolithium or Grignards a number of other metals were likewise tested as transmetalating agents, including copper, cerium, iron, ytterbium, zinc [2a–d]. Also the organomanganese chemistry has been studied extensively in the last 15 years [3] and these reagents, easily available from the organolithium and magnesium counterparts, have been engaged in coupling reactions with alkyl, vinyl and aryl derivatives [4], in acylation [5] and 1,2- [3c,6] and 1,4-addition [7] reactions. Their advantages with respect to other organometallics have been highlighted [3] in terms of high yields, no need of additives, high selectivity, smooth reaction conditions and ease of performance. Asymmetric induction promoted by nucleophilic addition to chiral aldehydes and ketones is a topic of great interest and has been used [8] for the construction of many useful chiral synthons in natural product synthesis. From the general point of view, organomanganese reagents look like very promising to perform such reactions since they are less basic and much more sensitive to steric effects than other organometallics [3c]. However until now there are very few reports about their use in these reactions with aldehydes [6,9] and to date only one paper has appeared [10] on the addition to cycloalkyl ketones.

2. Results and discussion

Herein we report a throughout study on the 1,2 addition of organomanganese halides RMnCl and of

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0022-328X/01/$ - see front matter
PII: S0022-328X(00)00902-5

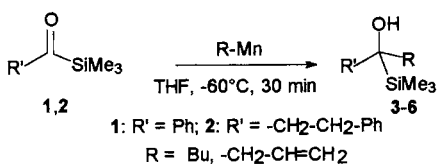
organomanganates R_3MnMet (Met = Li, MgCl) to α-chiral carbonyl compounds with the aim of studying their effectiveness in the diastereoselective 1,2-addition. Since acylsilanes are known to exhibit exceptional diastereofacial preferences in nucleophilic additions (1,2-asymmetric induction) and behave as aldehyde equivalents via stereospecific protiodesilylation with F^- [11], we thought it worthwhile to investigate the addition reaction of organomanganese reagents to these compounds and to compare their reaction behaviour whenever possible to that of the corresponding aldehydes. The 1,2-addition to the carbonyl moiety of several simple achiral acylsilanes is reported in Table 1.

The reactions proceeded smoothly to give the expected carbinols **3**–**6** in good yields, and organomanganese halides (entries 1, 3, 5, 7) and pivaloyloxyorganomanganates (entries 2, 4, 6, 8) proved to be equally effective. The choice of these latter reagents was dictated by previous observations [12] suggesting high reactivity, and better propensity to induce stereoselection of organomanganates with respect to the organomanganese derivatives. Worth noting even in the case of the acylsilane **2** (entries 5–8) prone to undergo easily enolization, this side reaction did not occur in view of the poorly basic character of the organomanganese reagents.

The high yields and the absence of enolization of compound **2** prompted us to engage in these reactions a racemic α-chiral acylsilane (**7**) and the corresponding 2-phenylpropanal (**8**), one of the carbonyl compounds studied most extensively for investigation of 1,2-asymmetric induction.

The relevant results are reported in Table 2 together with the literature data concerning the nucleophilic additions of organometallic reagents.

Table 1
Addition of organomanganese compounds to acylsilanes



1,2 3-6

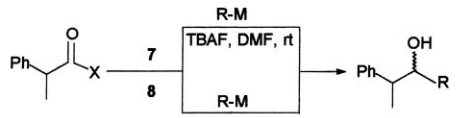
1: R' = Ph; 2: R' = -CH_2-CH_2-Ph
R = Bu, -CH_2-CH=CH_2

Entry	Substrate	RM	Product	Yield %
1	1	BuMnCl	3	85
2		(PivO)2(Bu)MnLi		95
3		(Allyl)MnCl	4	95
4		(PivO)2(Allyl)MnMgCl		95
5	2	BuMnCl	5	84
6		(PivO)2(Bu)MnLi		78
7		(Allyl)MnCl	6	95
8		(PivO)2(Allyl)MnMgCl		95

Efficient delivery of the alkyl and allyl ligands to the carbonyl moiety of **7** and **8** could be observed irrespective of the nature of the organomanganese reagent. Nucleophilic addition to these compounds having no ability to be chelated, produced predominantly, in full agreement with previous findings [11], the *syn*-diastereomer according to a Cram's open-chain model. As far as the stereochemical outcome, addition to the α-chiral acylsilane **7** occurred (entries 1, 2, 4, 5, 7, 8) with remarkable Cram selectivity, the diastereomeric ratios (d.r.) ranging from 92:8 to >99:1. These results are consistent with those obtained by Ohno [11] using organolithium and Grignard reagents (entries 3, 6, 9). Noteworthy are the ratios of the Cram:anti-Cram products found in the addition to the model α-chiral aldehyde **8**. Whereas addition of *n*-BuLi (entry 13) [13] and of *n*-BuMgBr (entry 12) [14] takes place with moderate stereoselectivities typically in the d.r. range 89:11–87:13, a significant increase of diastereoselectivity (97:3, 98:2) close to that observed in the case of **7**, was found (entries 10, 11) with organomanganese reagents. Again in the case of methyl transfer from MeMnCl and $(PivO)_2MeMnLi$ to **8**, better Cram selectivities were obtained compared to MeMgBr (entry 17). Interestingly the best diastereoselectivity (94:6) obtained so far by Reetz (entry 18) via 'slow addition' of a salt-free MeLi solution [13] could be obtained by simply using MeMnCl (entry 15) whereas with $(PivO)_2MeMnLi$ a significant improvement of the d.r. (98:2) was observed (entry 16). Even the presence of non transferable bulky ligands at magnesium, though to some extent beneficial [15], still led (entries 14, 19) to diastereoselectivities not exceeding those obtained with the Mn-based reagents. Finally only a slight increase in the diastereoselective ratios could be noticed by using organomanganates. According to the above results in the addition to α-chiral carbonyl derivatives the use of even very simple organomanganese reagents in most cases overcomes the necessity of bulky ligands at the metal center and renders less crucial the presence of a trialkylsilyl moiety attached to the carbonyl function for increasing diastereoselectivity. Only in the case of the more reactive allylating organomanganese reagents (entries 20, 21) the presence of the trimethysilyl moiety is still highly beneficial.

Next we moved towards more structurally complex chiral acylsilanes and aldehydes to investigate the diastereoselective induction by organomanganese derivatives in the case of carbonyl compounds with multiple functional groups in which several chelate structures are a priori feasible. The homochiral acylsilane **12** derived from lactic acid [16], the corresponding O–Bn protected lactic aldehyde **13** and glyceraldehyde acetonide **14** containing alkoxy groups that are constrained conformationally by incorporation in a ring, were subjected to nucleophilic additions of organomanganese reagents.

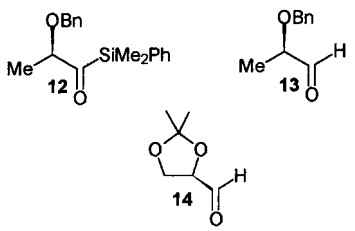
Table 2
Addition of organometallic reagents to **7** and **8**



7 : X = Me3Si 8 : X = H 9-11

Entry	Substrate	R-M	Product	Yield %[a]	Product ratio[b] [*syn*/*anti*]
1	**7**	BuMnCl	**9**	75	>99/1
2		(PivO)2(Bu)MnLi		80	>99/1
3		BuLi		91	>99/1[c]
4		MeMnCl	**10**	95	96/4
5		(PivO)2MeMnLi		94	97/3
6		MeLi		91	>97/3[c]
7		(Allyl)MnCl	**11**	90	93/7
8		(PivO)2(Allyl)MnLi		90	96/4
9		(Allyl)MgBr		85	92/8[c]
10	**8**	BuMnCl	**9**	70	97/3
11		(PivO)2(Bu)MnLi		80	98/2
12		BuMgBr		89	87/13[d]
13		BuLi		77	89/11[e]
14		BuMgOPiv		68	95/5[f]
15		MeMnCl	**10**	75	94/6
16		(PivO)2MeMnLi		85	98/2
17		MeMgI		64	72/28[d]
18		MeLi		65	94/6[e]
19		MeMgOPiv		87	94/6[f]
20		(Allyl)MnCl	**11**	83	76/24
21		(PivO)2(Allyl)MnMgCl		80	82/18
22		(Allyl)MgBr		92	63/37[c]

[a]Yields of isolated products.[b]Determined by 1H-NMR and GC chromatography on chiral capillary columnn (see experimental).
[c] Ref 11. [d]Ref 14. [e]Ref 13. [f]Ref 15.



The allylation reaction performed on **12** led to formation in good yields of the expected homoallylic alcohols **16**. Stereospecific desilylation followed by column chromatography afforded separation of the two diastereoisomers of **18** in a 66% combined yield. The absolute configuration determined by comparison with polarimetric and NMR data from the literature [17], indicated that the *anti*-product was the major component (*syn*:*anti* = 25:75). Delivery of the *n*-butyl ligand from both organomanganese halide and organomanganate to acylsilane **12** afforded on the other hand, after desilylation of **17** the two diastereoisomers of **19** which were separated in 60% combined yield. The prevalence of the *anti* alcohol (*syn*:*anti* = 10:90) was proved again by comparison of the polarimetric and ^{1}H-NMR data with those from the literature [18].

In comparison with **12**, aldehyde **13** showed no stereoselectivity, equimolar mixtures of the *syn* and of the *anti* diastereomers being obtained under identical reaction conditions. However this is not unprecedented since it is known [19] that the diastereoselectivity in the addition to 2-hydroxypropanal dramatically depends on the protecting group of the hydroxyl functionality, the reaction solvent and the steric demand of the organometallic reagent so that both the *syn* or the *anti* adducts can largely prevail. The differences in the d.r. ratios between **12** and **13**, highlight on the other hand the crucial role played by the R_3Si moiety in determining the stereochemical outcome. In the case of 2,3-*O*-isopropylideneglyceraldehyde (**14**), a synthetically useful chiral starting material for the construction of optically active organic molecules, prediction of the stereochemistry of nucleophilic addition is very difficult. Usually with organometallic compounds such as Grignard, organolithium or organozinc reagents, *anti*-addition products prevail [20] and the degree of diastereoselectivity with few exceptions is not satisfactory from a synthetic point of view. Addition of organomanganese reagents to **14** occurred with high yields and the degree of diastereoselectivity was consistently better than that reported in the literature for other organometallic reagents [21]. Thus allylation of **14** with organomanganese compounds and organomanganates led (Table 3, entries 5, 6) to adduct **20** as a 20:80 mixture of the diastereomeric alcohols *syn*-**20** and *anti*-**20**, and 80% total yield. The diastereomeric ratio was determined by isolation of each isomer with column chromatography on silica gel and by comparison of their ^{1}H- and ^{13}C-NMR spectra with that published [22]. In analogous way the stereochemical outcome of the addition of the *n*-butyl ligand leading to a 15:85 mixture of the diastereomeric alcohols *syn*-**21** and *anti*-**21**, and 76% total yield was established after separation by comparison with the literature data (Table 3, entries 7, 8) [23]. The *anti* diastereoselectivity, observed in the reaction of **12** with organomanganese reagents may be ascribed to the predominance of the Felkin–Ahn conformation **A** if one assumes that the OBn group is the 'large' substituent at the asymmetric α-carbon. The predominant formation of the *anti*-diastereomeric reaction product observed in the case of **14** also amounts to application of Felkin' s model for asymmetric induction. Chelation to oxygen, which has been proved to be effective in the case of manganese derivatives [24] might be operational in this case in stabilizing the β-chelate conformer **B**.

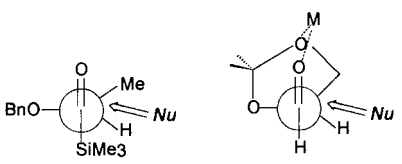
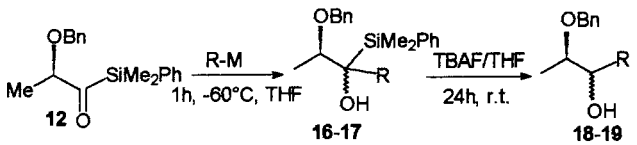
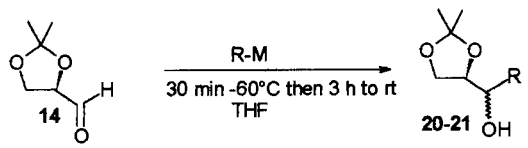


Table 3
Addition of organomanganese compounds to homochiral acylsilanes and aldehydes



Entry	R-M	Product	*syn*/*anti* ratios		Yield
1	CH_2=CH-CH_2-MgBr/ $MnCl_4Li_2$/BuLi/Pivalic acid	**18**	30	70	(66%)
2	CH_2=CH-CH_2-MgBr/ $MnCl_4Li_2$		25	75	(66%)
3	BuLi/ $MnCl_4Li_2$/Pivalic acid	**19**	10	90	(60%)
4	BuLi/ $MnCl_4Li_2$		10	90	(60%)
					
5	CH_2=CH-CH_2-MgBr/ $MnCl_4Li_2$/BuLi/Pivalic acid	**20**	22	78	(76%)
6	CH_2=CH-CH_2-MgBr/ $MnCl_4Li_2$		20	80	(80%)
7	BuLi/ $MnCl_4Li_2$/Pivalic acid	**21**	15	85	(76%)
8	BuLi/ $MnCl_4Li_2$		15	85	(72%)

3. Conclusions

In summary, this study demonstrates that the exploration of the potential ability of organomanganese reagents to be engaged in stereoselective additions can be rewarding. The preliminary picture which evolves is likely to be one of complementarity, i.e. organomanganese reagents can favourably compete with other organometallics in providing an useful tool for asymmetric synthesis. Indeed more extensive work is necessary under different reaction conditions, varying the medium and the reaction temperature, and with different organic reaction partners. These studies are currently underway.

4. Experimental

4.1. General reaction conditions

Moisture sensitive reactions were carried out in oven-dried (120°C) glassware under dry argon. Transfer of anhydrous solvents or mixtures was accomplished with the standard syringe/septum technique. THF was distilled just before use from benzophenone ketyl under argon. CH_2Cl_2 was passed through basic alumina and distilled from CaH_2 just prior to use. Other solvents were purified by standard procedures. Light petroleum refers to the fraction bp 40–60°C. The reactions were monitored by TLC on Baker-flex IB2-F silica gel plates. Column chromatography was performed with Merck 70–230 mesh silica gel 60. Preparative TLC was carried out on glass plates using a 1 mm layer of Merck silica gel Pf_{254}.^{1}H- and ^{13}C-NMR spectra were recorded using $CDCl_3$ solutions at 200, 300 MHz and 50.3, 75.4 MHz, respectively, on a Varian Gemini 200 and a Varian Gemini 300. Chemical shifts are reported in ppm relative to $CHCl_3$ (δ 7.23 ppm for ^{1}H and δ 77.0 ppm for ^{13}C). IR spectra were registered on a Perkin Elmer 257 and on a FT-IR Nicolet impact 400 spectrometers. Mass spectra were recorded on a VG 7070E at a ionising voltage of 70 eV. $[\alpha]_D$ values were taken on a Perkin

Elmer 341 polarimeter. Diastereomeric excesses were determined by gas chromatography with a chiral capillary column (SGE-25QC2/cydex-B 0.25).

4.2. Representative procedure

4.2.1. Method A

To a well stirred solution of the 'ate' complex $MnCl_2LiCl$, prepared from $MnCl_2$ (189 mg, 1.5 mmol) and LiCl (127 mg, 3.0 mmol) in anhydrous THF (3.6 ml), a 1.0 M solution of allylmagnesium bromide in THF (1.5 ml, 1.5 mmol) was added at −30°C. The reaction mixture was stirred for additional 20 min at −10°C, than 1.0 mmol of the appropriate substrate in THF (1 ml) was added at −60°C. The reaction mixture was kept at −60°C for 30 min then left to reach room temperature (r.t.) and after 3 h the disappearence of the starting compounds was monitored by TLC. After dilution with ether (20 ml) the reaction mixture was quenched with 1 M HCl. After separation of the organic phase and washing of the aqueous solution with ether (2 × 15 ml) the organic phases were put together, washed with water and dried over $MgSO_4$. After removing the organic solvent in vacuo, the expected product was purified by silica gel flash chromatography.

4.2.2. Method B

To a well stirred solution of the 'ate' complex $MnCl_2LiCl$, prepared from $MnCl_2$ (317 mg, 2.52 mmol) and LiCl (214 mg, 5.04 mmol) in anhydrous THF (7.0 ml), a 1.6 M solution of *n*-butyllithium in hexane (3.15 ml, 5.04 mmol) was added at −30°C. The reaction mixture was stirred for additional 20 min at −10°C. The temperature was lowered at −30°C and pivalic acid (515 mg, 5.04 mmol) in THF (3.0 ml) was added. After 10 min at −10°C the temperature was lowered at −30°C and allylmagnesium bromide (2.52 ml, 2.52 mmol) was added. After further 20 min at −10°C, 1.0 mmol of the appropriate substrate in THF (1 ml) was added at −60°C. The reaction mixture was kept at −60°C for 30 min then left to reach r.t. and after 3 h the disappearence of the starting compounds was monitored by TLC. The reaction was quenched and the product isolated following the above reported procedure.

4.3. Characterization of representative products

4.3.1. 1-Phenyl-1-(trimethylsilyl)-1-pentanol (**3**)

^{1}H-NMR (200 MHz, $CDCl_3$) δ: 0.00 (s, 9H, $Si(CH_3)_3$), 0.90 (t, 3H, $J = 7.5$ Hz, CH_3), 1.20–2.10 (m, 6H, $3CH_2$), 7.10–7.45 (m, 5H, CH–Ar) ppm. ^{13}C-NMR (50.3 MHz, $CDCl_3$) δ: −4.0 (3C, $Si(CH_3)_3$), 12.8 (3C, *C*HAr), 14.2 (1C, CH_3), 23.3 (1C, CH_2CH_3), 24.0 (1C, CCH_2CH_2), 36.5 (1C, CCH_2), 72.8 (1C, *C*Ph), 125.0 (1C, *C*Ar), 128.0 (2C, *C*HAr) ppm. GC-MS (*m*/*e*): 236 [M^+], 218 [$M^+ - H_2O$], 117 [$M^+ - SiOC_5H_{14}$], 104 (117 − CH), 73 ($SiMe_3$).

4.3.2. 1-Phenyl-3-(trimethylsilyl)-3-heptanol (**5**)

^{1}H-NMR (200 MHz, $CDCl_3$) δ: 0.20 (s, 9H, $Si(CH_3)_3$), 1.00 (t, 3H, $J = 7.5$ Hz, CH_3), 1.28 (s, 1H, O*H*), 1.34–1.48 (m, 4H, $CH_2CH_2CH_3$), 1.68–1.79 (m, 2H, $C(OH)CH_2$), 1.88–1.99 (m, 2H,CH_2CH_2Ph), 2.65–2.85 (m, 2H, CH_2Ph), 7.20–7.45 (m, 5H, C*H*Ar) ppm. ^{13}C-NMR (50.3 MHz, $CDCl_3$) δ: −2.60 (3C, $Si(CH_3)_3$), 14.3 (1C, CH_3), 23.7 (1C, CH_2CH_3), 26.2 (1C, $CH_2CH_2CH_3$), 29.9 (1C, CH_2Ph), 37.8 (1C, $C(OH)CH_2$), 39.9 (1C, $PhCH_2CH_2C(OH)$), 68.9 (1C, *C*(OH)), 128.5, 128.4, 125.9 (5C, *C*HAr), 143.0 (1C, *C*Ar) ppm. GC-MS (*m*/*e*): 264 [M^+], 246 [$M^+ - H_2O$], 231 (246 − CH_3), 91 (C_7H_7), 73 ($SiMe_3$).

4.3.3. 1-Phenyl-3-(trimethylsilyl)-5-hexen-3-ol (**6**)

Colorless liquid, ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 0.15 (s, 9H, $Si(CH_3)_3$), 1.80–1.95 (m, 2H, $PhCH_2$), 2.45 (d, 2H, $J = 7.41$ Hz, $CH_2CH{=}CH_2$), 2.65–2.80 (m, 2H, $PhCH_2CH_2$), 5.10–5.30 (m, 2H, $CH{=}CH_2$), 5.75–6.00 (m, 1H, $CH{=}CH_2$), 7.10–7.40 (m, 5H, C*H*Ar) ppm. ^{13}C-NMR (50.3 MHz, $CDCl_3$) δ: −2.5 (3C, $Si(CH_3)_3$), 30.4 (1C, CH_2Ph), 40.5 (1C, CH_2CH_2Ph), 42.3 (1C, $CH_2CH{=}CH$), 68.1 (1C, *C*(OH)), 118.9 (1C, $CH{=}CH_2$), 128.7, 128.6, 126.0 (5C, *C*HAr), 134.0 (1C, $CH{=}CH_2$), 143.0 (1C, *C*Ar) ppm. GC-MS (*m*/*e*): 231 [$M^+ - H_2O$], 91 (C_7H_7), 73 ($SiMe_3$).

4.3.4. 2-(Benzyloxy)-3-[dimethyl(phenyl)silyl]-5-hexen-3-ol (**16**)

Colorless liquid, $[\alpha]_D = 52.7$ ($c = 2.00$, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: major diastereosiomer: 0.60 (s, 3H, CH_3Si), 0.61 (s, 3H, CH_3Si), 1.33 (d, 3H, $J = 6.3$ Hz, CH_3–CH). Minor diastereoisomer: 0.62 (s, 3H, CH_3Si), 0.64 (s, 3H, CH_3Si), 1.36 (d, 3H, $J = 6.3$ Hz, CH_3–CH). The following signals were overlapped: 2.44 (bs, 2H, OH), 2.51–2.80 (m, 4H, $CH_2CH{=}$), 3.82 (q, 2H, $J = 6.3$ Hz, C*H*–CH_3), 4.50–4-91 (m, 4H, CH_2O), 5.19–5.29 (m, 4H, $2CH_2{=}$), 5.95–6.24 (m, 2H, CH=), 7.41–7.82 (m, 20H, Ar–H) ppm. ^{13}C-NMR (50.3 MHz, $CDCl_3$) δ: major diastereoisomer: −3.71 (CH_3Si), −3.43 (CH_3Si), 79.47 (CH–CH_3). Minor diastereoisomer: −3.27 (CH_3Si), −3.11 (CH_3Si), 81.18 (CH–CH_3). The following signals were overlapped: 13.41 (CH_3), 38.85 ($CH_2CH{=}$), 70.86 (OCH_2), 71.14 (C^{IV}), 111.11 ($CH_2{=}$), 127.36–134.25 (6 ArCH), 134.65 (CH=), 137.37 (ArC^{IV}), 138.47 (ArC^{IV}), ppm. MS (*m*/*e*): 325 [$M^+ - CH_3$], 249 [$M^+ - CH_2Ph$], 135 ($SiMe_2Ph$), 91 (CH_2Ph). After desilylation with TBAF in THF at r.t. for 24 h and separation by column chromatography on silica gel (eluent CH_2Cl_2) the two diastereoisomers *syn*-**18** and *anti*-**18** were obtained whose analytical and spectra data were consistent with literature data [17].

*4.3.5. 2-(Benzyloxy)-3-[dimethyl(phenyl)silyl]-3-heptanol (**17**)*

Obtained as a colorless liquid after column chromatography on silica gel (eluent petroleum/diethyl ether, 6:1), $[\alpha]_D = 15.5$ ($c = 1.00$, $CHCl_3$). ^{1}H-NMR (200 MHz, $CDCl_3$) δ: 0.60–0.80 (t, 3H, $J = 7.0$ Hz, CH_3CH_2), 1.10–1.35 (m + s, 7H, $CH_2CH_2CH_2$ + OH), 1.30 (d, $J = 6.8$ Hz, 3H, CH_3–CH), 4.10 (q, 1H, $J = 6.8$ Hz, CH–CH_3), 4.60 (d, $J = 11.4$ Hz, 1H, OCH_2Ph), 4.70 (d, $J = 11.4$ Hz, 1H, OCH_2Ph), 7.20–7.60 (m, 10H, ArH) ppm. ^{13}C-NMR (50.3 MHz, $CDCl_3$) δ: −0.41 (CH_3Si), −0.45 (CH_3Si), 13.30 (CH_3), 13.68 (CH_3), 22.80 (CH_2), 23.60 (CH_2), 33.50 (CH_2), 71.10 (OCH_2Ph), 73.00 (C^{IV}), 78.80 (CHO), 134.10 (ArC^{IV}), 137.60 (ArC^{IV}), 126.20–135.20 (6 ArCH) ppm. MS (m/e): 356 [M^+], 341 [$M^+ - CH_3$], 297 [$M^+ - Ph$], 221 [$M^+ - SiMe_2Ph$], 135 ($SiMe_2Ph$), 91 (CH_2Ph). After desilylation as for **16**, and purification by column chromatography on silica gel (eluent CH_2Cl_2) the *anti*-**19** was obtained whose analytical and spectra data were consistent with literature data [18].

Acknowledgements

This work has been supported by University of Bologna (Funds for Selected Research Topics, A.A. 1999–2001), by the MURST ex-60% e.f. 2000, and by the National Project Stereoselezione in Sintesi Organica Metodologie ed Applicazioni 1999–2001).

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