was stirred for 1.5 h and evaporated. 30 ml of $CHCl_3$ saturated with ammonia was added to the residue. The crystalline precipitate was filtered off and washed with ether. 1.78 g (97%) of the ammonium salt of acid **12** was obtained, m.p. 134—135°C, δP 41.8 (D_2O). ^1H NMR spectrum (δ, *J*, Hz; CD_3OD): 4.23 (d, 3H, CH_3P, $^2J_{PH}$=12.9); 1.81 (dt, 2H, PCH_2, $^2J_{PH}$=13.8, $^3J_{HH}$=8.0); 2.51—2.64 (m, 2H, CH_2CO); 3.68 (s, 3H, OCH_3), 4.97 (broad s, 4H, NH_4). The salt was dissolved in 50 ml of EtOH and passed through a column with KU-2 cationite (H^+-form). The solvent was distilled off, and the residue was dried *in vacuo* (2 h, 1 Torr, 45—50°C). 1.6 g (97%) of acid **12** was obtained in the form of a thick colorless oil, n_D^{20} 1.4732.

Compound **12** was obtained using a similar technique in a 96% yield from propenylphosphinate **4**. The spectral parameters of the compound prepared from phosphinates **2** and **4** coincide.

The acid **13** was synthesized in a similar way using EtOH (see Tables 2 and 3), n_D^{20} 1.4686.

Methyl(2-oxamoylethyl)phosphinic acid (14). Dry HCl was passed through a solution of 6.1 g (0.02 mole) of unsaturated phosphinate **4** in 30 ml of ether at 0°C for 0.5 h. 0.36 ml (0.02 mole) of H_2O in 10 ml of THF was added and the reaction mixture was stirred for 1 h. The solution was concentrated *in vacuo*, and the crystalline residue was washed with diethyl ether and dried *in vacuo* over P_2O_5 to give 3.5 g (98%) of acid **14**, m.p. 88°C, ^{31}P NMR (DMSO): δ 49.5.

Methyl(2-oxaloethyl)phosphinic acid (15). To 3.6 g (0.02 mole) of oxamoylsubstituted phosphinic acid **14**, 30 ml of concentrated HCl was added. The reaction mixture was refluxed, then the water was evaporated *in vacuo*. Acetone was added to the residue, NH_4Cl was filtered off, and the residue was dried *in vacuo*. 3.5 g (quantitative yield) of ketoacid **15** was obtained as a pale yellow oil, ^{31}P NMR (acetone-d_6): δ 55.3.

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Received June 25, 1992.

Diastereoselective addition of organomanganese compounds to α-alkoxysubstituted propanals

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Reactions of organomanganese compounds R^1MnI (R^1 = Ph, 4-MeC_6H_4-, Me, Bu, *n*-C_7H_{15}, BuC≡C, PhC≡C), prepared from R^1Li and MnI_2 in Et_2O, with aldehydes $MeCH(OR^2)CHO$ (R^2 = CH_2Ph, CH_2OMe, CH_2OCH_2Ph) afford *threo*-alcohols $MeCH(OR^2)CH(OH)R^1$ with high diastereoselectivity. The interactions of phenylmanganese derivatives PhMnX (X = Cl, Br, I), Ph_2Mn, and Ph_3MnLi with 2-benzyloxypropanal were used as examples for studying the influence of reagent and solvent nature on addition diastereoselectivity.

Key words: organomanganese compounds, chiral alkoxyaldehydes, 2-benzyloxypropanal, condensation, diastereoselectivity.

Diastereoselective addition of organometallic reagents to aldehydes is of great importance for preparation of stereoisomerically pure β- and γ-substituted secondary alcohols, which are valuable synthones for preparation of many natural, biologically active compounds.[1—4] Condensation of aldehydes having asymmetrical α- or β-

Translated from *Izvestiya Akademii Nauk, Seriya Khimicheskaya*, No. 1, pp. 178-181, January, 1993.

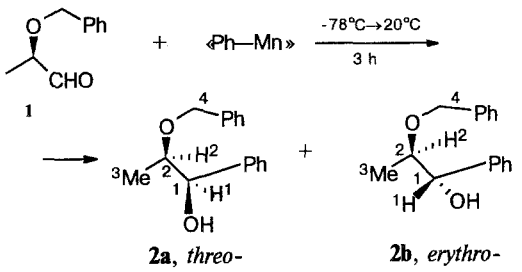
1066-5285/93/4201-0161 $12.50

carbon atoms (in particular, α- or β-alkoxyaldehydes) with organolithium and organomagnesium compounds is known to be of low stereoselectivity in most cases.[1,5] Organic derivatives of Mn(II) have recently been successfully used for creation of new carbon-carbon bonds in 1,2-addition to the aldehyde group,[6] as well as in 1,4-addition to α,β-enones[7] and enals.[8]

In this work we studied the diastereoselectivity of reactions of manganese σ-complexes with racemic O-benzyl, O-methoxymethyl, and O-benzyloxymethyl derivatives of 2-hydroxypropanal chosen as model aldehydes.

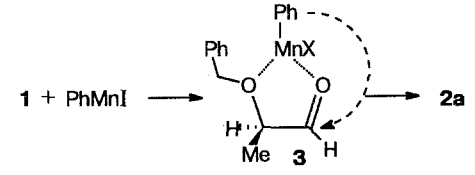
The starting organomanganese compounds were prepared *in situ* by interaction of organolithium compounds or Grignard reagents with manganese halides at −10÷−5°C.[9]

Table 1 presents the results of studying the reactions of 2-benzyloxypropanal (**1**) with phenylmanganese compounds:



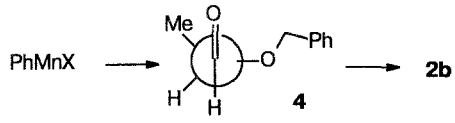
As follows from Table 1, interaction of racemic aldehyde **1** with PhMnI prepared from PhLi and MnI_2 in Et_2O leads to *threo*-isomeric alcohol **2a** in high yield and 95% stereoselectivity. PhMnI prepared from PhMgBr reacts even more selectively, but the yield of **2a** is not more than 40%. In the ^1H NMR spectra of diastereomers **2a** and **2b** separated by preparative HPLC, the coupling constants of the C(1), C(2) protons are 7.0 and 3.9 Hz, respectively, which evidences the *threo*-configuration of the main product **2a**.[10,11]

According to the literature data,[1,5,12] the predominant formation of *threo*-isomeric alcohols in reactions of organometallic compounds with α-alkoxyaldehydes is related to formation of chelate complexes of type **3**, where the nucleophilic attack takes place at the least sterically hindered side of the carbonyl group (Cram's "cyclic" model[12]):



On transition from PhMnI to PhMnBr, the ratio **2a**/**2b** decreases from 95:5 to 87:13, which is probably due to a decreased ability to form chelate **3** (for dihalides of magnesium and zinc the Lewis acidity is known[13] to decrease in the order: MI_2, MBr_2, MCl_2). The solvent nature exerts an even stronger influence on the diastereoselectivity. Thus, the reaction of PhMnI with aldehyde **1** in an Et_2O—THF mixture (1:2.5) gives the *erythro*-alcohol **2b** as the main product (**2a**/**2b** = 36:64). The predominating formation of **2b** is also observed with reagents prepared in the same solvent mixture from PhLi and $MnCl_2$ or Li_2MnCl_4 (Table 1, runs 5 and 6)*. In the presence of 15 vol.% DMF and HMPT, the portion of *erythro*-isomer **2b** grows even higher, although its content is never above 80%.

Thus, the *threo*-selectivity in the reaction of phenylmanganese halides with aldehyde **1** is lower the higher the solvation ability of the solvent to metal cations (the solvation ability is known[14] to decrease in the order: Et_2O, THF, DMF, HMPT). Decrease in donor properties of the solvent seems to impede the formation of **3** due to coordination of THF, DMF, and HMPT molecules with the manganese atom. Without complexing, conformation **4** of the substrate, where the $PhCH_2O$-C_α bond is perpendicular to the plane of aldehyde fragment, is the most reactive (the Felkin—Anh model[1,5,15]):



Diphenylmanganese and an «ate» complex of Ph_3MnLi prepared by treating Li_2MnCl_4 with 2 and 3

* Preparation of organomanganese compounds RMnCl from $MnCl_2$ and RLi or RMgBr in pure Et_2O cannot be carried out due to low solubility of $MnCl_2$.[9]

Table 1. Reactions of phenylmanganese derivatives with 2-benzyloxypropanal (**1**) (-78→20°C, 3 h, [reagent]$_0$: [**1**]$_0$ = 2:1)

Run	Reagent	Solvent	Yield (**2a**+**2b**), %	*threo* (**2a**): *erythro* (**2b**)[a]
1	PhMnI (PhLi + MnI_2)	Et_2O	86	95:5
2	PhMnI (PhMgBr + MnI_2)	Et_2O	36[b]	97:3
3	PhMnBr (PhLi + $MnBr_2$)	Et_2O	68	87:13
4	PhMnI (PhLi + MnI_2)	Et_2O—THF[c]	90	36:64
5	PhMnCl (PhLi + $MnCl_2$)	Et_2O—THF	81	35:65
6	PhMnCl (PhLi + Li_2MnCl_4)	Et_2O—THF	60	30:70
7	PhMnCl (PhLi + Li_2MnCl_4)	Et_2O—THF—DMF[d]	70	26:74
8	PhMnCl (PhLi + Li_2MnCl_4)	Et_2O—THF—HMPT[e]	72	23:77
9	Ph_2Mn (2PhLi + Li_2MnCl_4)	Et_2O—THF	61	38:62
10	Ph_3MnLi(3PhLi+Li_2MnCl_4)	Et_2O—THF	43[b]	49:51
11	PhMgBr	Et_2O	80	84:16
12	PhLi	Et_2O	57	39:61

[a] According to HPLC. [b] Noticeable resinification of the reaction mixture was observed. [c] Hereinafter, THF—Et_2O 2.5:1. [d] 15% DMF (v/v).[e] 15% HMPT (v/v).

equiv. of PhLi, respectively (Et_2O — THF, 1 : 2.5), react with aldehyde **1** similarly to PhMnCl to give chiefly the *erythro*-alcohol **2b**, however with a lower stereoselectivity. The content of **2b** decreases from 72 to 51% on transition from PhMnCl to Ph_2Mn and then to Ph_3MnLi. In addition, if Ph_3MnLi is used, marked resinification of the reaction mixture is observed.

Similarly to PhMnI, interaction of PhMgBr with **1** gives mainly the *threo*-alcohol **2a**; with PhMgBr instead of PhMnI the reaction selectivity decreases from 95 to 80%. On changing to PhLi, the main condensation product is the *erythro*-isomer **2b** (Table 1, run 12). The much lower tendency of organolithium compounds to form products under chelate control as compared to Grignard reagents is well known.[16,17]

The regularities found in the study of reactions with PhMnI, PhMgBr, and PhLi are also manifested for the corresponding methyl derivatives (Table 2, runs 1—4) (Scheme 1).

Thus, MeMnI prepared from MeLi and MnI_2 in Et_2O reacts with **1** to give the *threo*-isomeric alcohol **5a** as nearly the only product. MeMgI as well as MeZnI react in a similar way but with lower selectivity. On transition to MeLi a reversal in stereoselectivity is observed. In ^1H NMR spectra of diastereomers **5a** and **5b** separated by means of preparative HPLC, the coupling constants of C(1) and C(2) protons are 6.3 and 3.3 Hz, respectively.[10,11]

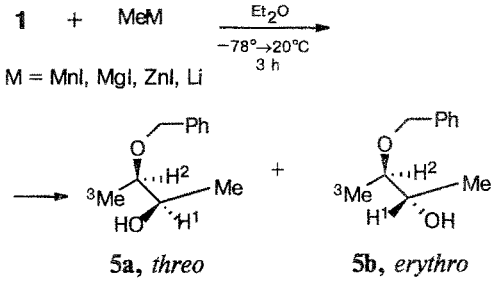
Other manganese derivatives of the RMnI type were prepared by treating MnI_2 with organolithium compounds in Et_2O. As follows from Table 2 (runs 5—9), the corresponding *threo*-isomeric alcohols **6a—10a** are formed with high stereoselectivity in reactions of *p*-tolyl-, butyl-, heptyl-, 1-hexinyl-, and phenylethynylmanganese iodide with **1** (Scheme 2).

The *threo*-configuration of **6a-10a** follows from a comparison of coupling constants of C(1) and C(2) protons (6.1—7.8 Hz) with those in the spectra of *threo*-isomers **2a** and **5a** which are of the same magnitude. In addition, in the ^{13}C NMR spectra of **2a** and **5a-10a** the signals of the C(3) atoms are in the range of 15.16 to 15.66 ppm, whereas the corresponding signals for *erythro*-isomers are in the range of 13.45 to 13.81 ppm.[11]

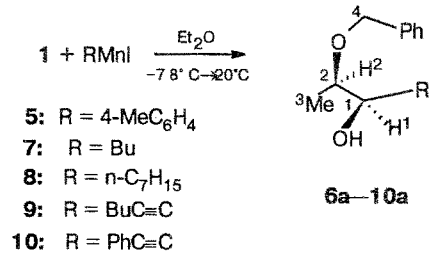
Under the conditions studied, arylmanganese σ-complexes with 4-methoxy- and 2,5-dimethoxyphenyl substituents do not react with **1**. Condensation of **1** with allyl derivatives $CH_2{=}CHCH_2MnX$ leads to formation of a nearly equimolar mixture of diastereomeric 2-benzyloxy-5-hexen-3-ols (**11a,b**) (THF, X=Cl) (Table 2, run 13).

Apart from the O-benzyl derivative of α-hydroxypropanal, the reactions of its O-methoxymethyl (**12**) and O-benzyloxymethyl analogs (**13**) with PhMnI were carried out. Interaction of PhMnI with aldehydes **12**, **13** proceeds with high stereoselectivity to give the *threo*-alcohols **14a**, **15a** (**14a—14b**, 94:6; **15a—15b**, 95:5) in 46 and 64% yield, respectively. Removal of methoxymethyl and benzyloxymethyl protective groups in compounds **14a**, **15a** leads to diol **16** which is identical to the

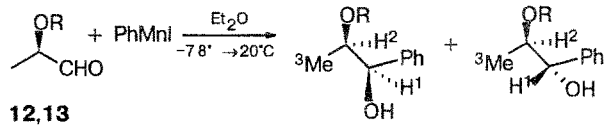
Scheme 1

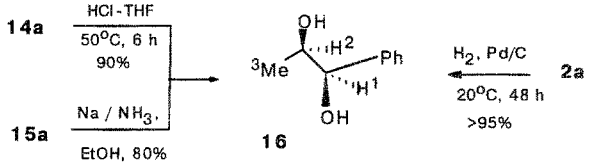


Scheme 2



hydrogenation product of the *threo*-isomer **2a** containing a benzyl fragment:





To conclude, the reactions of aryl-, alkyl-, and alkynyl- σ-complexes of Mn(II) prepared from MnI_2 and organolithium compounds in Et_2O with α-alkoxyaldehydes can serve as a convenient and stereoselective procedure for the preparation of *threo*- β-alkoxysubstituted secondary alcohols.

Experimental

GLC analysis was carried out using a Chrom-5 chromatograph equipped with a flame-ionization detector, in a flow of helium (40 ml/min); column size 1.2m x 3mm, 5% SE-30 on Inerton-Super. The ratio of *threo*- and *erythro*-isomers was determined by high performance liquid chromatography using a

Table 2. Reactions of organomanganese compounds with 2-benzyloxypropanal (**1**)
(Et_2O, −78→20°C, 3 h, $[reagent]_0 : [1]_0 = 2 : 1$)

Run	Reagent	Reaction prducts	Yield %	[a] *threo* (**a**): *erythro* (**b**)
1	MeMnI	**5a,b**	88	93:7
2	MeMgI	**5a,b**	80	85:15
3	MeZnI[b]	**5a,b**	52	87:13
4	MeLi	**5a,b**	60	27:73
5	4-MeC_6H_4MnI	**6a,b**	94	93:7
6	BuMnI	**7a,b**	69	>97:3
7	n-$C_7H_{15}MnI$	**8a,b**	90	>97:3
8	BuC≡CMnI	**6a,b**	71	>97:3
9	PhC≡CMnI	**10a,b**	36	95:5
10	4-$MeOC_6H_4MnI$	—[c]	—	—
11	2,5-$(MeO)_2C_6H_3MnI$	—[d]	—	—
12	CH_2=$CHCH_2MnI$[e]	—[f]	—	—
13	CH_2=$CHCH_2MnCl$[g]	**11a,b**	70	50:50

[a] According to HPLC. [b] Prepared from MeLi and ZnI_2 in Et_2O (0°C, 40 min). [c] Only aldehyde **1** and MeOPh were isolated. [d] Only aldehyde **1** and 1,4-$(MeO)_2C_6H_4$ were isolated. [e] Prepared from CH_2=$CHCH_2MgBr$ and MnI_2 in Et_2O at −78°C. [f] Marked resinification of the reaction mixture was observed. [g] Prepared from CH_2=$CHCH_2MgCl$ and Li_2MnCl_4 in THF at −78°C.

DuPont 8800 liquid chromatograph equipped with a refractometer; a Zorba X-Sil (250 x 4.6 mm) column was used, the mobile phase was hexane—ethyl acetate, 80:20—95:5, the flow rate was 1.0 ml/min, pressure $95 \cdot 10^5$ Pa. ^1H and ^{13}C NMR spectra were recorded using a Bruker AM 300 spectrometer (300 MHz) in $CDCl_3$ with tetramethylsilane as the internal standard. IR spectra were obtained with an UR-20 spectrophotometer in thin films.

Ethereal solutions of organolithium and organo-magnesium compounds, MnI_2,[9] Li_2MnCl_4 (as a 0.8 *M* THF solution)[9] were prepared according to the known procedures. 2-Benzyloxypropanal,[18] 2-methoxymethoxypropanal,[19] and 2-benzyloxymethoxypropanal[19] were prepared by reduction of the corresponding ethyl lactates with diisobuthyl aluminium hydride. All reactions were carried out under dry argon. Et_2O and THF were distilled over $LiAlH_4$ before use.

Reactions of organomanganese compounds with α-alkoxyaldehydes. To a suspension of 0.618 g (2 mmol) of MnI_2 in 8 ml of Et_2O with stirring and cooling to -10°C was added 2.5 ml (2 mmol) of a 0.8 *M* ether solution of PhLi. The mixture was stirred for 40 min at −10÷−5°C. After cooling to −78°C a solution of 0.164 g (1 mmol) of **1** in 1 ml of Et_2O was added. The reaction mixture was stirred for 1 h at −78°C, heated to room temperature in 3 h, hydrolyzed with 30 ml of 6% HCl, and extracted with Et_2O (3 × 15 ml). The combined ether extracts were washed with water (10 ml), dried with $MgSO_4$, and concentrated. By means of column chromatography (silica gel L 40/100; hexane—Et_2O, 3:1), 0.208 g (86%) of **1-phenyl-2-benzyloxypropan-1-ol (2a,b)** as a mixture (95:5) of *threo*- and *erythro*-isomers was isolated.* ^1H NMR spectrum (δ, *J*, Hz): of **2a**: 0.95 (d, 3H, Me, J = 6.2), 3.15 (br.s, 1H, OH), 3.52 (dq, 1H, CH, J_1 = 7, J_2 = 6.2), 4.36 (d, 1H, CH, J = 7), 4.37 d and 4.56 d, (2H, CH_2, J_{AB} = 11.5), 7.25 (m, 10H, arom.); **2b**: 1.17 (d, 3H, Me, J = 6.3), 3.05 (br.s, 1H, OH), 3.3 (d q, 1H, CH, J_1 = 3.9, J_2 = 6.3), 4.59 d and 4.69 d (2H, CH_2, J_{AB} = 11.9), 4.96 (d, 1H, CH, J = 3.9), 7.3—7.5 (m, 10H, arom.). ^{13}C NMR spectrum (δ): **of 2a**: 79.93 (d, C-1), 78.26 (d, C-2), 15.61 (q, C-3), 71.25 (t, C-4), 127.24 (d), 127.61 (d), 127.91 (d), 128.15 (d), 128.31 (d), 128.49 (d), 138.25 (s), 140.73 (s) (Ar); **2b**: 78.77 (d, C-1), 75.11 (d, C-2), 13.45 (q, C-3), 70.87 (t, C-4); 126.27 (d), 127.21 (d), 127.60 (d), 127.80 (d), 128.05 (d), 128.34 (d), 138.35 (s), 140.82 (s) (Ar). IR spectrum (ν, cm^{-1}): 3450, 3080, 3045, 1610, 1500, 760, 720, 700.

Reactions of organomanganese compounds RMnX (R = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 2,5-$(MeO)_2C_6H_3$, Me, Bu, *n*-C_7H_{15}, CH_2=$CHCH_2$, BuC≡C, PhC≡C; X = Cl, Br, I), Ph_2Mn, Ph_3MnLi with aldehydes MeCH(OR)CHO (R = CH_2Ph, CH_2OMe, CH_2OCH_2Ph) were carried out using similar procedures.

3-Benzyloxybutan-2-ol (5a,b)*.[16] ^1H NMR spectrum (δ, *J*, Hz) of **5a**: 1.15 d and 1.17 (d, 6H, Me, J= 6,3), 2.68 (br.s, 1H, OH), 3.31 d q and 3.61 d q (2H, CH, J_1= J_2= 6.3), 4.44 d and 4.67 d (2H, CH, J_{AB}= 11.5), 7.28 (m, 5H, arom.); **5b**: 1.06 d and 1.08 d (6H, Me, J= 6.3), 2.26 (br.s, 1H, OH), 3.41 d q and 3.84 d q (2H, CH, J_1= 3.3, J_2= 6.3), 4.42 d and 4.55 d (2H, CH_2, J_{AB}= 11.8), 7.25 (m, 5H, arom.). ^{13}C NMR spectrum (δ) of **5a**: 71.26 (d, C-1), 80.26 (d, C-2), 15.46 (q, C-3), 71.12 (t, C-4), 18.62 (q, Me); 127.84 (d), 128.54 (d), 138.45 (s) (arom.); **5b**: 69.30 (d, C-1), 78.31 (d, C-2), 13.54 (q, C-3), 70.77 (t, C-4), 17.77 (q, Me), 127.65 (d), 128.46 (d), 138.68 (s) (arom.). IR spectrum (ν, cm^{-1}): 3450, 3080, 3045, 1610, 1505, 760, 720.

1-(*p*-Tolyl)-2-benzyloxypropan-1-ol (6a,b). ^1H NMR spectrum of **6a** (δ, *J*, Hz): 0.99 (d, 3H, Me, J= 6.1), 2.25 (s, 3H, Me), 3.15 (br.s, 1H, OH), 3.55 (d q, 1H, CH, J_1= 7.8, J_2= 6.2), 4.35 (d, 1H, CH, J= 7.8), 4.42 d and 4.53 d (2H, CH_2, J_{AB}= 11.3), 7.06 d and 7.17 d (4H, arom., J_{AB}= 7.8), 7.3 (m, 5H, arom.). ^{13}C NMR spectrum (δ) of **6a**: 80.13 (d, C-1), 78.26 (d, C-2), 15.64 (q, C-3), 71.32 (t, C-4), 21.23 (q, Me), 127.24 (d), 127.30 (d), 128.57 (d), 129.09 (d), 137.65 (s), 138.31 (s, arom.); **6b**: 78.84 (d, C-1), 75.10 (d, C-2), 13.47 (q, C-3), 71.03 (t, C-4), 21.23 (q, Me). IR spectrum (ν, cm^{-1}): 3450, 3080, 3045, 1610, 1500, 760, 720, 700.

***threo*-2-Benzyloxyheptan-3-ol (7a).**[16] ^1H NMR spectrum (δ, *J*, Hz): 1.32 (t, 3H, Me, J= 7.1), 1.1 (d, 3H, Me, J= 5.9), 1.15—1.45 (m, 6H, CH_2), 2.55 (br.s, 1H, OH), 3.29 (d q, 1H, CH, J_1= 6.3, J_2= 5.9), 3.33 (m, 1H, CH), 4.33 d and 4.58 d (2H, CH_2, J_{AB}= 11.5), 7.22 (m, 5H, arom.). ^{13}C NMR spectrum (δ): 74.96 (d, C-1), 78.49 (d, C-2), 15.58 (q, C-3), 71.04 (t, C-4), 14.02 (q, Me), 22.79 (t), 27.79 (t), 32.67 (t, CH_2), 127.70 (d), 127.79 (d), 128.45 (d), 138.58 (s, arom.). IR spectrum (ν, cm^{-1}): 3450, 3080, 3045, 1610, 1505, 760, 720.

***threo*-2-Benzyloxydecan-3-ol (8a).** ^1H NMR spectrum (δ, *J*, Hz): 0.78 (t, 3H, Me, J= 7.2), 1.08 (d, 3H, Me, J= 5.9), 1.1-1.45 (m, 12H, CH_2), 2.5 (br.s, 1H, OH), 3.26 (d q, 1H, CH, J_1= 6.3, J_2= 5.9), 3.3 (m, 1H, CH), 4.32 d and 4.55 d (2H, CH_2, J_{AB}= 11.4), 7.2 (m, 5H, arom.). ^{13}C NMR spectrum (δ): 75.05 (d, C-1), 78.58 (d, C-2), 15.66 (q, C-3), 71.09 (t, C-4), 14.16 (q, Me), 22.73 (t), 25.66 (t), 29.33 (t), 29.77 (t), 31.93 (t), 33.03 (t, CH_2), 127.79 (d), 127.85 (d), 128.52 (d), 138.51 (s, arom.). IR spectrum (ν, cm^{-1}): 3450, 3080, 3050, 1610, 1505, 760, 720.

***threo*-2-Benzyloxy-4-nonyn-3-ol (9a).** ^1H NMR spectrum

* The diastereomers were separated by means of preparative HPLC.

(δ, J, Hz): 0.9 (t, 3H, Me, J= 6), 1.18 (d, 3H, Me, J= 6), 1.22—1.5 (m, 6H, CH_2), 2.55 (br.s, 1H, OH), 3.37 (d q, 1H, CH, J_1= 6.2, J_1= 6), 3.42 (m, 1H, CH), 4.43 d and 4.67 d (2H, CH_2, J_{AB}= 11.5), 7.35 (m, 5H, arom.). ^{13}C NMR spectrum (δ): 75.02 (d, C-1), 78.55 (d, C-2), 15.64 (q, C-3), 71.09 (t, C-4), 71.06 (s), 77.10 (s, C≡C), 14.08 (q, Me), 22.83 (t), 27.82 (t), 32.71 (t, CH_2), 127.77 (d), 127.85 (d), 128.51 (d), 138.51 (s, arom.). IR spectrum (ν, cm^{-1}): 3440, 3090, 3060, 1610, 1495, 735, 695.

1-Phenyl-4-benzyloxy-1-pentyn-3-ol (10a,b). ^{1}H NMR spectrum of **10a** (δ, J, Hz): 1.45 (d, 3H, Me, J= 6.2), 2.85 (br.s, 1H, OH), 3.72 (d q, 1H, CH, J_1= 6.6, J_2= 6.2), 4.47 (d, 1H, CH, J= 6.6), 4.6 d and 4.72 d (2H, CH_2, J_{AB}= 11.6), 7.2—7.45 (m, 10H, arom.). ^{13}C NMR spectrum (δ) of **10a**: 65.87 (d, C-1), 77.21 (d, C-2), 15.16 (q, C-3), 70.71 (t, C-4), 84.83 (s), 86.58 (s, C≡C), 126.83 (d), 127.24 (d), 127.45 (d), 130.73 (d), 137.14 (s, arom.); **10b**: 64.65 (d, C-1), 76.15 (d, C-2), 13.81 (q, C-3), 70.10 (t, C-4). IR spectrum (ν, cm^{-1}): 3400, 3065, 3030, 2230, 1595, 1490, 755, 735, 690.

2-Benzyloxy-5-hexen-3-ol (11a,b).[16] ^{1}H NMR spectrum (δ, J, Hz): 1.12 d and 1.14 d (3H, Me, J= 6.2), 2.0—2.3 (m, 2H, CH_2C=), 3.3—3.55 (m, 2H, CH), 3.36 d and 4.59 d (2H, CH_2, J_{AB}= 11.5), 4.43 d and 4.54 d (2H, CH_2, J_{AB}= 11.8), 4.95—5.15 (m, 2H, CH_2=), 5.7-5.9 (m, 1H, CH=), 7.25 (m, 5H, arom.). ^{13}C NMR spectrum (δ): 13.93 q and 15.51 q (Me), 37.07 t and 37.64 t (CH_2C=), 70.89 t and 71.12 t (CH_2), 72.74 d and 74.36 d (CHOH), 77.31 d and 77.59 d (CH), 117.22 t and 117.54 t (CH_2=), 134.90 d and 135.02 d (CH=), 127.71 (d), 127.79 (d), 127.85 (d), 128.51 (d), 138.48 (s), 138.65 (s, arom.). IR spectrum (ν, cm^{-1}): 3450, 3080, 3045, 1650, 1600, 1510, 1010, 930, 750, 715.

1-Phenyl-2-methoxymethoxypropan-1-ol (14a,b). ^{1}H NMR spectrum of **14a** (δ, J, Hz): 1.05 (d, 3H, Me, J= 6.3), 3.38 (s, 3H, Me), 3.38 (br.s, 1H, OH), 3.78 (d q, 1H, CH, J_1= 7.3, J_2= 6.3), 4.45 (d, 1H, CH, J= 7.3), 4.7 d and 4.78 d (2H, CH_2, J_{AB}= 6.8), 7.3 (m, 5H, arom.). ^{13}C NMR spectrum of **14a** (δ): 79.56 (d, C-1), 78.37 (d, C-2), 17.08 (q, C-3), 96.19 (t, CH_2), 55.67 (q, OMe), 127.19 (d), 127.96 (d), 128.40 (d), 140.96 (s, arom.); **14b**: 77.38 (d, C-1), 76.00 (d, C-2), 14.28 (q, C-3), 95.35 (t, CH_2), 55.67 (q, OMe). IR spectrum (ν, cm^{-1}): 3430, 3080, 3065, 3035, 1605, 1500, 735, 700.

1-Phenyl-2-benzyloxymethoxypropan-1-ol (15a,b). ^{1}H NMR spectrum (δ, J, Hz) of **15a**: 1.13 (d, 3H, Me, J = 6.3), 3.42 (br.s, 1H, OH), 3.9 (d q, 1H, CH, J_1= 7.1, J_2 = 6.3), 4.52 (d, 1H, CH, J = 7.1), 4.61 (s, 2H, CH_2Ph), 4.85 d and 4.92 d (2H, CH_2, J_{AB}= 7), 7.45 (m, 5H, arom.). ^{13}C NMR spectrum (δ): 79.23 (d, C-1), 78.23 (d, C-2), 16.96 (q, C-3), 93.97 (t, CH_2), 69.85 (t, CH_2Ph), 127.10 (d), 127.85 (d), 127.92 (d), 128.35 (d), 128.49 (d), 137.58 (s), 140.93 (s, arom.); **15b**: 75.89 (d, C-2), 14.16 (q, C-3), 96.13 (t, CH_2), 69.70 (t, CH_2Ph). IR spectrum (ν, cm^{-1}): 3430, 3090, 3065, 3030, 1605, 1495, 735, 700.

***threo*-1-Phenylpropan-1,2-diol (16)**,[20] m.p. 55°C. ^{1}H NMR spectrum (δ, J, Hz): 1.08 (d, 3H, Me, J= 6.5), 2.5 (br.s, 1H, OH), 4.0 (d q, 1H, CH, J_1= 4.3, J_2= 6.3), 4.67 (d, 1H, CH, J= 4.3), 7.45 (m, 5H, arom.). ^{13}C NMR spectrum (δ): 77.62 (d, C-1), 71.40 (d, C-2), 17.35 (q, C-3), 126.72 (d), 127.91 (d), 128.35 (d), 140.44 (s, arom.). IR spectrum (ν, cm^{-1}): 3480, 3050, 3035, 1605, 1495, 760, 700.

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Received April 4, 1992