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A Useful Application of Benzyl Trichloroacetimidate for the Benzylation of Alcohols

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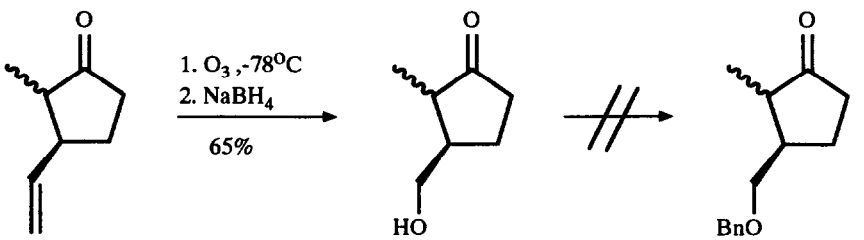
Abstract - Primary, secondary and tertiary alcohols, which are sensitive under basic or acidic reaction conditions, can be *O*-benzylated under mild acidic reaction conditions using benzyl 2,2,2-trichloroacetimidate as the benzylation agent. Chiral substrates, which have a tendency towards racemization under basic reaction conditions, can be benzylated without any loss of chirality.

I. Introduction

Benzyl ethers play a central role as persistent protecting groups in natural product synthesis.[1] In the course of an enantioconvergent total synthesis[2] of vitamin D,[3] the preparation of 3-benzyloxymethyl-2-methyl cyclopentanone (**3a**) as the ring D building block was taken aim at. 3-Hydroxymethyl-2-methyl cyclopentanone (*rac*-**2a**) was prepared by ozonolysis of 2-methyl-3-vinyl cyclopentanone (*rac*-**1a**)[4] and subsequent reduction of the 3-formyl group in 65% yield. By applying various methods for the benzylation which have been reported[5] towards 3-hydroxymethyl-2-methyl cyclopentanone (*rac*-**2a**), the corresponding benzyl ether *rac*-**3a** was not obtainable in any case.



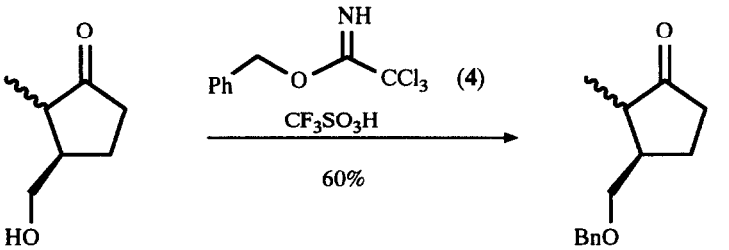
rac-**1** *rac*-**2a** *rac*-**3a**

This result is in agreement with those reported by Denmark for attempts to benzylate 3-hydroxymethyl cyclohexanones.[6]

Benzyl trichloroacetimidate (**4**) seems to be suitable for the benzylation of those base sensitive alcohols, since this reagent has been successfully employed for the benzylation of carbohydrates,[7,8] lactams[9] and β-hydroxy esters.[10] Trichloroacetimidates were first prepared and thoroughly investigated by Cramer and his group in the late fifties.[11]

II. Results and Discussion

Benzyl trichloroacetimidate (**4**) was prepared on a 300 g scale by a base catalyzed addition of benzyl alcohol to trichloroacetonitrile.[11a] Treatment of 3-hydroxymethyl-2-methyl cyclopentanone (*rac*-**2a**) with 2 equivalents of benzyl trichloroacetimidate (**4**) and catalytic amounts (55 mol%) of trifluoromethanesulfonic acid (TFMSA) yielded 3-benzyloxymethyl-2-methyl cyclopentanone (**3a**) (60%) besides trichloroacetamide (**6**), which could be separated easily by filtration or - when reactions were run on a smaller scale - by column filtration.



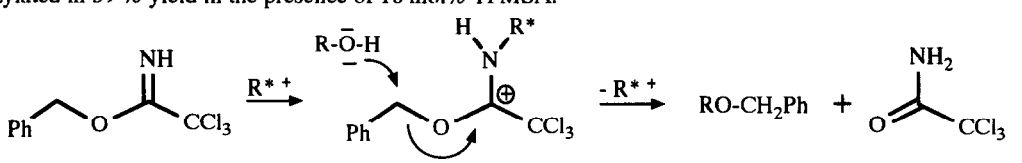
rac-**2a** *rac*-**3a**

In order to investigate the scope and limitations of benzylations using benzyl trichloroacetimidate (**4**) as the benzylating agent, several alcohols, which could not be benzylated under classical conditions in our laboratory,[5] were treated with benzyl trichloroacetimidate (**4**) under the above described conditions.

The benzylation of the alcohols **2b-g** under classical conditions[5] failed for various reasons:

Like 3-hydroxymethyl-2-methyl cyclopentanone (*rac*-**2a**) the alcohols **2d** and **2f** underwent a decomposition which was based on undesired aldol condensations. Alcohol *rac*-**2c** suffers a desilylation at the trimethylsilyl acetylene function, alcohol **2e** was subject to retro aldol cleavage, whereas alcohol *rac*-**2g** underwent a base induced epoxidation. Last but not least, the tertiary cyclopropanol *rac*-**2b**, which is stable under basic reaction conditions, could not be benzylated most probably due to steric reasons.

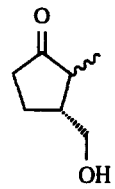
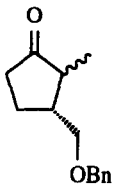
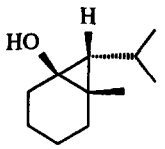
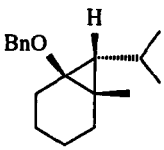
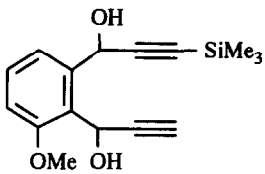
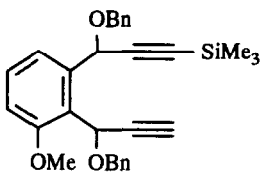
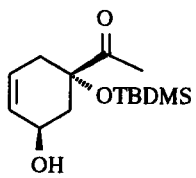
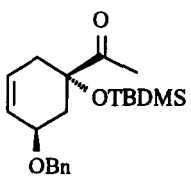
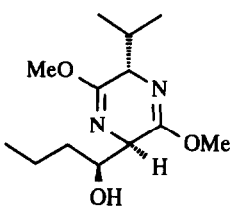
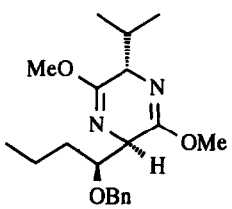
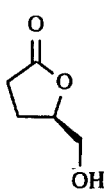
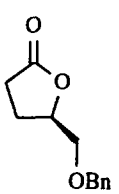
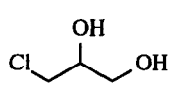
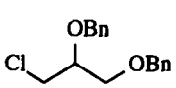
All these different alcohols could be benzylated with benzyl trichloroacetimidate (**4**) under the reaction conditions described above. The best results were obtained with trimethylsilyl trifluoromethanesulfonate (TMS-OTf) as an acidic catalyst whereas the yields which were obtained by the use of TFMSA or boron trifluoride etherate were only moderate. It is noteworthy that the tertiary cyclopropanol *rac*-**2b**, which is very lable towards acid, could be benzylated in 39 % yield in the presence of 10 mol% TFMSA.



4 R* = H, $SiMe_3$ **5** **3** **6**

According to mechanistic studies by Cramer and Hennrich[11b] the following mechanism can be proposed: In the first step benzyl trichloroacetimidate (**4**) is protonated or silylated yielding the cation **5**. This species is a very reactive electrophile and reacts rapidly with the alcohols **2** to the benzyl ethers **3** and trichloroacetamide **6**. In this step the proton becomes liberated and can return into the catalytic cycle.

Since the benzyl ethers **3** and trichloroactamide can be easily separated on a larger scale by filtration and since trichloroacetamide (**6**) can be recycled into trichloroacetonitrile by simple dehydratisation,[12] the use of benzyl trichloroacetimidate (**4**) can also be recommended for all kinds of benzylations on a larger scale.

2, 3	Alcohol 2	Benzyl ether 3	Yield (%)	Catalyst (mol%)
rac-**a**			60	TFMSA (55)
rac-**b**			39	TFMSA (10)
rac-**c**			45	TFMSA (4)
d			61	TMS-OTf (20)
e			67	TMS-OTf (20)
f			73	TMS-OTf (20)
rac-**g**			78	TMS-OTf (10)

EXPERIMENTAL

Infrared (IR) spectra were obtained using a Perkin-Elmer 298 spectrometer. NMR spectra were obtained using a Varian XL 200 or a VXR 200 spectrometer for ^1H and ^{13}C NMR. Chemical shifts are given in parts per million (δ) using tetramethylsilane as an internal standard for ^1H- and ^{13}C NMR. Mass spectra were recorded on Varian MAT 731 or 311 A spectrometers. Optical rotations were measured on a Perkin Elmer Mod. 141 polarimeter. TLC analyses were performed on Polygram Sil G/UV_{254} silica gel plates. Silica gel (0.030-0.060 mm) from Baker was used for flash chromatography. Combustion analyses were carried out by the microanalytical laboratory of the University of Göttingen. All reactions were carried out under a nitrogen or argon atmosphere. All reagents were purified and dried if necessary before using. Benzyl trichloroacetimidate (**4**) was prepared according to Cramer's protocol.[11a] 2-methyl-3-vinyl cyclopentanone (*rac*-**1a**) was obtained as described by Quinkert et al. .[4] The alcohols **2d** and **2e** were prepared according to ref. [13] and [14]. The alcohol *rac*-**2b** was obtained by a reductive desulfurization of the corresponding β-(phenylthio)ketone.[15] The alcohol *rac*-**2c** was prepared in three steps starting from *N,N*-diethylamido methoxysalicylate, whereas the alcohol **2f** was prepared from *L*-glutamic acid by diazotization and subsequent reduction of the carboxylic group.[16]

trans-3-Formyl-2-methylcyclopentanone: At -70°C a stream of ozone and oxygen was bubbled through a stirred solution of 5.0 g (40 mmol) *rac*-**1** in 80 ml CH_2Cl_2 and 20 ml methanol until a slight blue coloring indicated an excess of ozone. The ozone was removed with a stream of oxygen, 15 ml dimethyl sulfide were added and stirring was continued for 30 min at -70°C and for 3 h at room temp. . The solution was concentrated by removing most of the solvent at 30°C/100 Torr and the residue was filtered through silica gel (30 g) with diethyl ether. The diethyl ether was removed at 20°C/80 Torr yielding 4.90 g (97%) *trans*-3-formyl-2-methylcyclopentanone, which was used directly for the next step. - *trans*:*cis* = 9:1. - R_f = 0.38 (diethyl ether). - **IR (neat):** ν = 1735 (C=O), 1715 cm^{-1} (H-C=O). - **^1H NMR (200 MHz, $CDCl_3$):** δ = 1.17 (d, J = 7 Hz; 3H, CH_3), 1.85 - 2.80 (m; 6H, CH and CH_2), 9.85 (d, J = 2 Hz; 1H, *trans*-CHO), 9.94 (d, J = 2 Hz; 1H, *cis*-CHO). - **$C_7H_{10}O_2$ (126.2)** calc. C, 66.65; H, 7.99, found C, 66.43; H, 8.12%.

trans-3-Hydroxymethyl-2-methylcyclopentanone (rac-2a): To a stirred solution of 4.78 g (38 mmol) *trans*-3-formyl-2-methylcyclopentanone in 40 ml THF, a solution of 0.36 g (9.5 mmol) sodium borohydride in 10 ml ethanol was added slowly at 0°C and stirring was continued for additional 30 min. The solvent was removed at 30°C/12 Torr, the residue was suspended in 30 ml diethyl ether and 1 *N* HCl was added dropwise until the solid compounds were dissolved. The organic layer was dried with $MgSO_4$, the solvent was removed at 30°C/ 12 Torr and the residue was purified by flash chromatography with diethyl ether on silica gel (70 g). 3.16 g (65%) *rac*-**2a** were obtained as a colorless oil. - *trans*:*cis* = 10:1. - R_f = 0.26. - **IR (neat):** ν = 3420 (OH), 1730 cm^{-1} (C=O). - **^1H NMR (200 MHz, $CDCl_3$):** δ = 1.08 and 1.13 (2 d, J = 7 Hz; 3H, *cis*- and *trans*-CH_3), 1.30-2.52 (m; 7H, CH_2, CH and OH), 3.81 (AB-system, J_{AB} = 11 Hz; 2H, CH_2OH). - **^{13}C NMR (50.3 MHz, $CDCl_3$):** δ = 12.94 (CH_3), 23.62 (O=C-$\underline{C}H_2$-CH_2), 35.90 (O=C-CH_2-$\underline{C}H_2$), 41.53 and 46.79 (CH_2), 64.22 (CH_2OH), 221.91 (C=O). - **$C_7H_{12}O_2$ (128.1)** calc. C, 65.58; H, 9.44, found C, 65.42; H, 9.57%.

trans-3-Benzyloxymethyl-2-methyl cyclopentanone (rac-3a): To a solution of 0.77 g (6 mmol) 3-hydroxymethyl-2-methyl cyclopentanone (*rac*-**2a**) in 25 ml CH_2Cl_2 and 5 ml THF 3.03 g (12 mmol) benzyl trichloroacetimidate (**4**) and 0.3 ml (3.4 mmol) of trifluoromethanesulfonic acid (TFMSA) were added at 0°C. After stirring for 2 h 15 ml CH_2Cl_2 and 15 ml 3% aqueous NaOH were added. The organic layer was extracted three times with H_2O (25 ml each) and dried with $MgSO_4$.The solvent was removed in vacuo (20°C/50 Torr) and the crude benzyl ether *rac*-**3a** was purified by chromatography with diethyl ether/petroleum ether (1:2) on silica gel (30 g) yielding 0.79 g (60%) of the benzyl ether *rac*-**3a** as a pale yellow oil. - *trans*:*cis* = 6:1. - R_f = 0.31. - **IR (neat):** ν = 3075, 3045 and 3010 (aromat. C=C-H), 1730 (C=O), 1595 und 1580 (aromat. C=C), 1100 cm^{-1} (C-O). - **^1H NMR (200 MHz, $CDCl_3$):** δ = 1.06 (d, J = 7 Hz; 3H, *cis*-CH_3), 1.16 (d, J = 7 Hz; 3H, *trans*-CH_3) ,1.50 - 2.50 (m; 6H, CH_2 and CH), 3.58 (m; 2H, O=C-O-CH_2), 4.35 and 4.43 (AB-system, J_{AB} = 8 Hz; 2H, C_6H_5-$\underline{C}H_2$), 7.20 - 7.45 (m; 5H, C_6H_5). - **^{13}C NMR (50.3 MHz, $CDCl_3$):** δ = 13.08 (CH_3), 24.44 and 37.14 (CH_2), 44.87 and 46.98 (CH), 72.32 and 73.21 (CH_2-O-CH_2), 127.48, 127.63 and 128.40 (*ortho*, *meta* und *para*-C), 138.32 (aromat. C-1), 220.81 (C=O). - **$C_{14}H_{18}O_2$ (218.2)** calc. C, 77.02; H, 8.32, found C, 76.86; H, 8.13%.

1-Benzyloxy-7-isopropyl-6-methylbicyclo[4.1.0]heptane (rac-3b): To a solution of 0.34 g (2 mmol) of the cyclopropanol *rac*-**2b** in 1 ml CH_2Cl_2 a solution of 0.95 g (4 mmol) benzyl trichloroacetimidate (**4**) in 3 ml cyclohexane was added at 0°C. 30 mg (0.2 mmol) of trifluoromethanesulfonic acid was added at the same temp. and stirring was continued at room temp. for 2 h. 20 ml Diethyl ether and 10 ml H_2O were added and the organic layer was extracted with 1 *N* aqueous NaOH, 1 *N* HCl and a sat. $NaHCO_3$-solution (5 ml each). The organic layer was dried with $MgSO_4$ and the solvent was removed in vacuo (25°C/20 Torr). The crude benzyl ether *rac*-**3b** was puri-

fied by chromatography with diethyl ether/petroleum ether (1:50) on silica gel (30 g) yielding 0.21 g (39%) of the benzyl ether *rac*-**3b** as a colorless oil. - R_f = 0.29. - **IR (neat):** ν = 735 and 690 cm^{-1} (δ_{CH} monosubst. aryl). - **^{1}H NMR (200 MHz, $CDCl_3$):** δ = 0.18 (d, J = 10 Hz; 1H, C-7-H), 0.86 and 0.95 (2 d, J = 6.9 Hz; 6H, $CH(CH_3)_2$), 1.12 (s; 3H, C-6-CH_3), 1.04 - 1.37 (m; 4H, CH_2), 1.46 - 1.60 (m; 2H, CH_2), 1.65 - 1.88 (m; 2H, CH_2), 2.02 - 2.09 (m; 1H, $CH(CH_3)_2$), 4.46 (AB-system, J_{AB} = 12.4 Hz; 2H, CH_2-C_6H_5), 6.97 - 7.30 (m; 5H, C_6H_5). - **^{13}C NMR (50.3 MHz, $CDCl_3$):** δ = 16.43 (C-6-CH_3), 21.66, 23.09, 28.67 and 34.31 (CH_2), 22.70 and 23.76 ($CH(CH_3)_2$), 24.11 (C-7), 24.12 (C-6), 35.31 (OCH_2), 39.44 ($CH(CH_3)_2$), 64.93 (C-1), 126.46, 126.88 and 128.15 (aromat. CH), 139.75 (aromat.C). - **MS (70 eV):** (*m/z*) = 258 (4 %, M^+), 215 (12 %, M^+ - C_3H_7), 167 (68 %, M^+ - C_7H_7), 91 (100 %, $C_7H_7^+$). - **$C_{18}H_{26}O$ (258.4)** calc. C, 83.67; H, 10.14, found C, 83.56; H, 10.06%.

General Procedure for the Preparation of the Benzyl Ethers 3c-g

2 mmol of the alcohols **2a-g** and 0.76 g (3 mmol) benzyl trichloroacetimidate (**4**) were dissolved in 40 ml CH_2Cl_2. After cooling to 0°C, 0.07 ml (0.4 mmol) trimethylsilyl trifluoromethanesulfonate (TMS-OTf) or 50 mg (0.33 mmol) trifluoromethanesulfonic acid (TFMSA) were added slowly and the reaction mixture was stirred 24 h at room temperature. After evaporating the solvent under reduced pressure, 30 ml of a petroleum ether/diethyl ether solution (6:1) were added to the residue and the crude slurry was filtered over a plug of silica gel to remove the formed trichloroacetamide and the silca gel was washed twice with a petroleum ether/diethyl ether solution (6:1). The combined organic fractions were washed with 20 ml of a saturated $NaHCO_3$ solution and with 20 ml of water. The organic solvent was evaporated under reduced pressure and the crude benzyl ethers **3c-g** were purified by flash chromatography or by bulb-to-bulb distillation.

3-(1-Benzyloxy-3-trimethylsilylprop-2-ynyl)-2-(1-benzyloxyprop-2-ynyl)anisole (rac-3c): To a solution of 1.15 g (4 mmol) of the diynediol *rac*-**2c** in 10 ml CH_2Cl_2 a solution of 4.40 g (16 mmol) benzyl trichloro acetimidate in 15 ml pentane and 50 mg (0.33 mmol) trifluoromethanesulfonic acid was added at 0°C. The stirred solution was allowed to warm up to room temp. and remained for 16 h at this temperature. Purification via flash chromatography on silica gel (80 g) with petroleum ether/diethyl ether (10:1) yielded 0.84 g (45%) of the bisbenzyl ether *rac*-**3c** as a pale yellow oil. *trans*:*cis* = 3:1. R_f = 0.21 (major diastereomer), 0.18 (minor diastereomer). - **IR (neat):** ν = 3260 (C≡C-H), 3040, 3020 and 3005 (aromat. C=C-H), 2150 (C≡C-Si), 2100 (C≡CH), 1590 and 1575 cm^{-1} (aromat. C=C). - **^{1}H NMR (200 MHz, $CDCl_3$):** δ = 0.07 [0.12] (s; 9H, $Si(CH_3)_3$), 2.31 [2.55] (d, ^4J = 2.4 Hz [^4J = 2.2 Hz]; 1H, C≡CH), 3.73 [3.75] (s; 3H, OCH_3), 4.28 - 4.81 (m; 4H, CH_2-C_6H_5), 5.89 [5.86] (d, ^4J = 2.4 Hz [^4J = 2.2 Hz]; 1H, 2-CH-O), 6.07 [5.89] (s; 1H, 3-CH-O), 7.12 - 7.46 (m; 13H, aromat. CH). - **^{13}C NMR (50.3 MHz, $CDCl_3$):** (major diastereomer) δ = -0.15 ($Si(CH_3)_3$), 55.89 (OCH_3), 62.38 and 67.54 (CH-O), 70.70 (C_6H_5-CH_2), 74.71 (C≡C-H), 82.17 (C≡C-H), 91.82 (C≡C-Si), 103.89 (C≡C-Si), 110.83 (C-6), 124.30 (C-2), 125.55 (C-4), 127.78, 128.03 and 128.90 (C_6H_5-CH_2), 132.58 (C-5), 135.28 (C-3), 137.41 and 137.82 (C_6H_5-CH_2, $C_{quart.}$), 156.66 (C-1). - **MS (70eV):** (m/z) = 379 (0.5%, M^+ - C_7H_7 + 2H), 254 (7%, M^+ - 2 C_7H_7O), 107 (18%, $C_7H_7O^+$), 91 (100%, $C_7H_7^+$). - **$C_{30}H_{32}O_3Si$ (468.7)** calc. C, 76.88; H, 6.88, found C, 76.91; H, 6.93%.

(+)-[1S,3R]-1-Acetyl-1-tert.butyldimethylsilyloxy-3-benzyloxy-cyclohex-4-ene (3d): 0.54g (2 mmol) **2d**, 0.76 g (3 mmol) benzyl trichloroacetimidate (**4**) and 0.07 ml (0.4 mmol) (TMS-OTf) were used. After flash chromatography with petroleum ether/diethyl ether (4:1) 0.44 g (61%) of **3d** were obtained as a colorless oil. R_f = 0.55. - $[\alpha]_D^{20}$ = + 58.94 (c = 1.023, $CHCl_3$). - **IR (neat):** ν = 3040 (C-H/phenyl), 1710 (C=O) cm^{-1}. - **^{1}H NMR (200 MHz, $CDCl_3$):** δ = 0.04 (s; 6H, $(CH_3)_3CSi(CH_3)_2O$), 0.85 (s; 9H, $(CH_3)_3CSi(CH_3)_2O$), 1.86 (dd, ^2J = 12.6 Hz, J_2 = 7.6 Hz; 1H, 2-H_{ax}), 1.99 - 2.19 (m; 2H, 2-H_{eq} and 6-H_{ax}), 2.21 (s; 3H, CH_3CO), 2.77 (ddddd, $^2J_1$ = 18.2 Hz, J_2 = 4.4 Hz, $^4J_3$ = ^4J = ^5J = 1.5 Hz; 1H, 6-H_{eq}), 4.23 (br. s; 1H, 3-H), 4.55 (s; 2H, $OCH_2C_6H_5$), 5.71-5.95 (m; 2H, 4-H and 5-H), 7.23-7.46 (m; 5H, C_6H_5). - **^{13}C NMR (50 MHz, $CDCl_3$):** δ = -3.19 and -2.81 ($(CH_3)_3CSi(CH_3)_2O$), 18.35 ($(CH_3)_3CSi(CH_3)_2O$), 24.16 (CH_3CO), 25.74 ($(CH_3)_3CSi(CH_3)_2O$), 33.39 and 38.02 (C-2 and C-6), 70.24 ($OCH_2C_6H_5$), 71.97 (C-3), 80.21 (C-1), 126.65, 126.99, 127.51, 127.63, 128.31 and 138.44 (C-4, C-5 and C_6H_5), 208.91 (CH_3CO). - **$C_{21}H_{31}O_3Si$ (359.6)** calc. C, 70.15; H, 8.69, found C, 70.28; H, 8.72%.

(1R)-1-[(2'S,5'R)-2',5'-Dihydro-5'-isopropyl-3',6'-dimethoxy-2'-pyrazinyl]-1-benzyloxy-butane (3e): 0.52 g (2 mmol) of the alcohol **2e**, 0.76 g (3 mmol) benzyl trichloroacetimidate (**4**) and 0.07 ml (0.4 mmol) (TMS-OTf) were used. Purification by flash chromatography on silica gel with petroleum ether/diethyl ether (4:1) yielded 0.47 g (67%) of **3e** as a colorless oil. R_f = 0.57. - $[\alpha]_D^{21}$ = -79.30 (c = 1.034, $CHCl_3$). - **IR (neat):** ν = 1690 cm^{-1} (C=N). - **^{1}H NMR (200 MHz, $CDCl_3$):** δ = 0.68 and 1.08 (2 d; J = 6.8 Hz; 3H each, $CH(CH_3)_2$), 0.93 (t, J = 7.4 Hz; 3H, 3-CH_3), 1.31-1.80 (m; 4H, $(CH_2)_2$), 2.32 (dsept, J_1 = 6.8 Hz and J_2 = 2.9 Hz; 1H, $CH(CH_3)_2$), 3.69 and 3.70 (2 s; 3H each, OCH_3), 3.87 (dt, J_1 = 6.8 Hz and J_2 = 2.5 Hz; 1H, 1-H), 3.96 (dd, J_1 = J_2 = 3.5 Hz; 1H, 5'-H), 4.06 (dd, J_1 = 3.5 Hz and J_2 = 2.3 Hz; 1H, 2'-H), 4.46 (s; 2H, OCH_2), 7.18-7.50 (m; 5H, C_6H_5). - **^{13}C NMR (50 MHz, $CDCl_3$):** δ = 14.24 and 16.44 ($CH(CH_3)_2$), 19.21 (C-4), 19.34 (C-3), 31.05 ($CH(CH_3)_2$), 33.31 (C-2), 52.18 and 52.39 (2 OCH_3), 58.32 and 60.35 (C-2' and C-5'), 72.52 (OCH_2), 80.00 (C-1), 127.42, 127.90, 128.10 and

138.52 (C_6H_5), 162.30 and 164.41 (C-3'and C-6'). - **$C_{20}H_{33}N_2O_3$ (349.5)** calc. C, 68.73; H, 9.52, found C, 68.61; H, 9.10%.

(3S)-5-Benzyloxypentane-4-olide (3f): 0.35 g (2 mmol) of **2f**, 0.76 g (3 mmol) benzyl trichloroacetimidate (**4**) and 0.07 ml (0.4 mmol) (TMS-OTf) were used. After flash chromatography with petroleum ether/diethyl ether (1:2) 0.30 g (73%) of **3f** were obtained as a colorless oil. R_f = 0.23. - $[\alpha]_D^{20}$ = + 14.10 (c = 1.00, $CHCl_3$). - **IR (neat):** ν = 3010 (C-H/phenyl), 1765 (C=O) cm^{-1}. - **^{1}H NMR (200 MHz, $CDCl_3$):** δ = 2.01 - 2.73 (m; 4H, $(CH_2)_2$), 3.58 and 3.69 (2dd, AB-part of an ABX-system, J_{AB} = 10.8 Hz ,J_{AX} = 4.2 Hz and J_{BX} = 3.2 Hz; 2H, CH_2O), 4.57 (s; 2H, $C\underline{H}_2C_6H_5$), 4.60 - 4.73 (m; 1H, 5-H), 7.23 - 7.44 (m; 5H, $CH_2C_6\underline{H}_5$). - **^{13}C NMR (50 MHz, $CDCl_3$):** δ = 24.07 and 28.38 (C-3 and C-4), 71.57 and 73.50 (CH_2O and $O\underline{C}H_2C_6H_5$), 78.99 (C-5), 127.58, 127.73, 128.43 and 137.68 ($CH_2\underline{C}_6H_5$), 177.35 (C=O). - **MS (70 ev):** (m/z) = 206 (12%, M^+), 91 (100%, $C_7H_7^+$). - **HRMS (70 ev):** calculated for **$C_{12}H_{14}O_3$** 206.2408, found 206.2408. - $C_{12}H_{14}O_3$ **(206.2)** calc. C, 69.89; H, 6.84, found C, 69.70; H, 6.79%.

2,3-Bisbenzyloxy-1-chloropropane (rac-3g): 0.21 g (2 mmol) of the alcohol *rac*-**2g**, 1.52 g (6 mmol) benzyl trichloroacetimidate (**4**) and 0.07 ml (0.4 mmol) (TMS-OTf) were used. After bulb-to-bulb distillation 0.45 g (78%) of *rac*-**3g** were obtained as a colorless oil. - **B.p.:** 140°C/0.1 Torr. - **IR (neat):** ν = 3010 (C-H/phenyl) cm^{-1}. - **^{1}H NMR (200 MHz, $CDCl_3$):** δ = 3.58 - 3.85 (m; 5H, 1- and 3-CH_2 and 2-CH), 4.54 (s; 2H, 3-OCH_2), 4.62 and 4.69 (AB-signal, $^2J_{AB}$ = 12 Hz; 2H, 2-OCH_2), 7.25 - 7.40 (m; 10H, $CH_2C_6\underline{H}_5$). - **^{13}C NMR (50 MHz, $CDCl_3$):** δ = 43.84 (C-1), 69.47 (C-3), 72.28 and 73.47 ($O\underline{C}H_2C_6H_5$ and 3-$O\underline{C}H_2C_6H_5$), 77.54 (C-2), 127.63, 127.69, 127.79, 128.38, 137.91 and 137.94 (2-C_6H_5). - **MS (70 ev):** (m/z) = 291 and 289 (1 and 3%, M^+), 200 and 198 (3 and 9%, M^+-C_7H_7), 91 (100%, $C_7H_7^+$). - **$C_{17}H_{19}ClO_2$ (290.8)** calc. C, 70.22; H, 6.89, found C, 69.68; H, 6.47%.

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