Pergamon

*Tetrahedron* Vol. 50, No. 33, pp. 9983-9988, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4020/94 $7.00+0.00

0040-4020(94)00576-1

# Convenient Oxidative Debenzylation Using Dimethyldioxirane

**RENÉ CSUK* AND PETRA DÖRR**

PHARMAZEUTISCH-CHEMISCHES INSTITUT, UNIVERSITÄT HEIDELBERG,

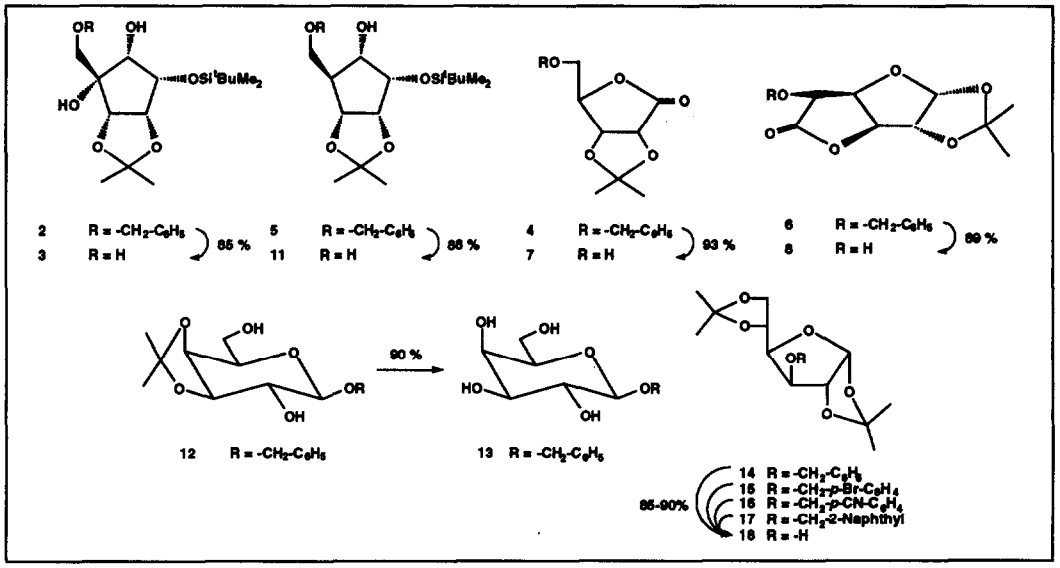
Im Neuenheimer Feld 364, D-69120 Heidelberg, Germany

***Abstract:*** *Substituted benzyl ethers are easily cleaved by their treatment with an excess of dimethyldioxirane; the corresponding alcohols are obtained in high yields.*

The proper choice and introduction of protective groups during synthesis as well as smooth and selective deprotection of functional groups are very often of high relevance for the success of a synthetic approach. [1] Benzyl ethers are amongst the oldest and most often used protective groups and many different methods [1] for their cleavage have been proposed, *inter alia* hydrogenations [2-6], reductions [7-9], the use of boron halides [10-12] and other strong Lewis acids [13-15] as well as of microorganisms [16] and by use of organometallic compounds.[17] Only a small number of oxidative cleavages, however, have been introduced like $CrO_3$/AcOH [18], $RuO_2$ [19], ozone [20] and electrolytic oxidations.[21] On the whole, the majority of these oxidative methods are restricted in their application and only a few can be used for synthetic transformations of complex natural products due to functional group incompatibility.

For the oxidation of vicinal secondary/tertiary diols the use of dimethyldioxirane (**1**) or trifluoromethylmethyldioxirane has been suggested.[22] According to this procedure, the polyhydroxylated cyclopentane derivative **2** was treated with an acetone solution of **1** but instead of an oxidation of the secondary hydroxyl group a clean debenzylation reaction was observed and the triol **3** was obtained in 85% yield.[23]

The insertion of oxygen from **1** into C-H bonds has been reported and recently *B. A. Marples et al.* described a dimethyldioxirane mediated debenzylation reaction.[24] On the other hand the successful epoxidation of perbenzylated carbohydrate derived cyclic enolethers without any accompanying debenzylation has been disclosed.[25]




This obvious controversy called for a more systematic investigation of the reaction of **1** with benzyl ethers in order to develop a synthetically useful oxidative debenzylation reaction.

Thus, in a typical experiment a dichloromethane solution of the educt was treated with an excess of an acetone solution of **1** at room temperature in the dark. Primary benzyl ethers as in **2**, **4** or **5** as well as benzyl ethers of secondary alcohols as exemplified for the reaction of **6** were cleaved. The products **3, 7** and **8** were obtained in 85%, 93% and 89% yield, respectively. This advantageous debenzylation method is compatible with silyl esters (**2** → **3, 9** →**10**[23] and **5** → **11**) and lactones (**4** → **7**, **6** → **8**). The isopropylidenated benzyl glycoside **12**, however, underwent no debenzylation under these conditions instead a clean cleavage of the 3,4-*O*-isopropylidene acetal is observed and **13** is obtained in 90% yield. This cleavage of the acetal moiety parallels the reported reaction of phenylacetaldehyde dimethylacetal with **1** to afford methyl phenyl acetate.[24]

Although it was assumed [24] that steric hinderance is important in retarding the reaction of **1** the debenzylation of 3-*O*-benzyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**14**) proceeded smoothly within 48 hours at room temperature;[26] however, almost no deprotection occurred when the reaction mixture was allowed to stand at -25° C. In addition, these deprotections are not confined to unsubstituted benzyl groups. Similarly the 4-bromobenzyl derivative **15**, the 4-cyanobenzyl analogue **16** as well as the 2-naphthylmethyl protected **17** afforded **18** in good yields.

## EXPERIMENTAL

The melting points are uncorrected (*Reichert* hot stage microscope), optical rotations were obtained using a Perkin-Elmer 243B polarimeter (1 cm micro-cell), NMR spectra (internal $Me_4Si$) were recorded using either a Bruker AM250 or a Varian XL300 instrument (δ given in ppm, *J* in Hz), IR spectra (film or KBr pellet) on a Perkin-Elmer 298 instrument, MS spectra were taken either on a MAT311A or a Varian-112S instrument; for elemental analysis a Foss-Heraeus Vario EL instrument was used. TLC was performed on silica gel (Merck 5554, detection by dipping in a solution containing 10% sulfuric acid (400 *ml*), ammonium molybdate (20 g) and cerium$^{(IV)}$ sulfate (20 mg) followed by heating to 150° C. The dichloromethane used throughout for all reactions was freshly distilled in succession from $P_4O_{10}$ and $K_2CO_3$; all reactions with **1** were performed in the dark.

**Dimethyldioxirane** (**1**).- The acetone solution of **1** was prepared according to a modified procedure given by *W. Adam et al.* [27]: A 4000 *ml* three-necked round-bottomed flask which contained a mixture of water (254 *ml*), acetone (192 *ml*, 2.62 mol) and sodium hydrogencarbonate (144 g) was equipped with a gas inlet tube which extended to the bottom of the flask, a facility to add solid caroate (potassium monoperoxosulfate, 310 g, 0.51 mol), and a cold-finger condenser assembly as designed by *M. Hudlicky* [28] for the large-scale generation of diazomethane.[29] This condenser was connected to a 500 *ml* receiving flask containing dry molecular sieves (4Å); this flask and the condenser were both cooled by means of a dry ice acetone bath to -78° C. A moderate stream of argon was passed through the reaction flask while the caroate was added in several portions; the reaction mixture was stirred vigorously during this addition. A total of 100-130 *ml* of effluent solution of **1** (*ca* 0.1 M) was collected in the receiving flask. This solution was stored at -25° in the dark and used within one week.

**General procedure for debenzylation.**- To a solution of the educt (1.0 mmol) in dry dichloromethane (10 *ml*) the acetone solution of **1** (60 *ml*) was added in six portions in the course of 48 h; the reaction mixture was stirred in the dark. The solvents were evaporated *in vacuo* and the residue subjected to chromatography (silica gel, hexanes/ ethyl acetate mixtures).

**(4a *R*)-1-*O*-(tert.-butyldimethylsilyl)-4a-carba-4,4a-dihydroxy-2,3-*O*-isopropylidene-α-D-ribofuranose** = (3a *S*, 4 *R*, 5 *R*, 6 *S*, 6a *R*)-6-tert.-butyldimethylsilyloxy-4-hydroxymethyl-2,2-dimethyl-tetrahydro-cyclopenta [1,3] dioxol-4,5-diol (**3**).- From (4a *R*)-5-*O*-benzyl-1-*O*-(tert.-butyldimethylsilyl)-4a-carba-4,4a-dihydroxy-2,3-*O*-isopropylidene-α-D-ribofuranose ( = (3a *S*, 4 *R*, 5 *R*, 6 *S*, 6a *R*)-4-benzyloxymethyl-6-tert.-butyldimethylsilyloxy-2,2-dimethyl-tetrahydro-cyclopenta [1,3] dioxol-4,5-diol) (**2**)[30] (0.43 g, 1.0 mmol) **3** (0.28 g, 85%) was obtained as an oil; $[\alpha]_D^{20}$ -25.5 (*c* 1.5, $CHCl_3$); IR (film): 3453*s*, 2930*s*, 2857*s*, 2362*w*, 1604*w*, 1585*w*, 1473*s*, 1463*s*, 1455*m*, 1377*s*, 1318*m*, 1257*s*, 1212*s*, 1162*s*, 1105*s*, 1049*s*; $^1$H-NMR (250 MHz, $CDCl_3$): 0.13 (*s*, 6 H, $SiMe_2$); 0.93 (*s*, 9 H, 3 x Me); 1.30 (*s*, 3 H, $Me^i$); 1.45 (*s*, 3 H, $Me^i$); 3.70-3.80 (*m*, 1 H); 3.90-4.10 (*m*, 1 H); 4.32 (*d*, *J* = 6.0 Hz, 1 H); 4.49 (*dd*, *J* = 4.6, 6.0 Hz, 1 H); $^{13}$C-NMR (75 MHz, $CDCl_3$): -4.50 (*q*, $SiMe_2$), 18.34 (*s*, $C_q$ of *t*-Bu); 24.02 (*q*, $Me^i$); 25.85 (*q*, 3 x Me of *t*-Bu); 25.89 (*q*, $Me^i$); 64.98 (*t*, C(5)); 77.14 (*s*, C(4)); 76.10, 76.61, 76.72, 81.76 (each *d*, C(1,2,3,4a)); 111.21 (*s*, $C_q^i$); MS (ei, 80 eV, 78°): 319 (4.3), 277 (30.6), 219 (13.0), 201 (58.9), 183 (20.3), 171 (24.7), 159 (16.7), 155 (19.7), 145 (14.1), 131 (14.7), 129 (58.5), 117 (42.2), 103 (42.8), 101 (11.1), 85 (27.6), 81 (14.6); Anal calcd. for $C_{15}H_{30}O_6Si$ (334.49): C, 53.86; H, 9.04; found: C, 53.92; H, 9.04.

**1,2-*O*-Isopropylidene-D-ribono-1,4-lactone** (**7**).- From 5-*O*-benzyl-1,2-*O*-isopropylidene-D-ribono-1,4-lactone (**4**)[31] (0.28 g, 1.0 mmol) **7** (0.18 g, 93%) was obtained; mp 136-138 °C, $[\alpha]_D^{20}$ -83.8 (*c* 1, $CHCl_3$) (Lit.:[32] mp 138-139 °C, $[\alpha]_D^{26}$ -84.2 (*c* 0.9, $CHCl_3$)).

**1,2-*O*-Isopropylidene-α-D-glucofuranurono-6,3-lactone** (**8**).- From 5-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranurono-6,3-lactone (**6**) (0.30 g, 0.98 mmol)[40] **8** (0.19 g, 89%) was obtained: mp 120-122 °C, $[\alpha]_D^{20}$ +44.1 (*c* 1, $CHCl_3$) (Lit.:[37] mp 121-123 °C, $[\alpha]_D^{20}$ +44.9 (*c* 1.2, $CHCl_3$)).

**(4a *S*)-1-*O*-(tert.-butyldimethylsilyl)-4a-carba-4a-hydroxy-2,3-*O*-isopropylidene-α-D-ribofuranose** = (3a *R*, 4 *S*, 5 *S*, 6 *S*, 6a *R*)-6-(tert.-butyldimethylsilyloxy)-4-hydroxymethyl-2,3-dimethyl-tetrahydro-cyclopenta [1,3] dioxol-5-ol (**11**).- From (4a *S*)-5-*O*-benzyl-1-*O*-(tert.-butyldimethylsilyl)-4a-carba-4a-hydroxy-2,3-O-isopropylidene-α-D-ribofuranose = (3a *R*, 4 *S*, 5 *S*, 6 *S*, 6a *R*)-4-benzyloxymethyl-6-tert.-butyldimethylsilyloxy-2,3-dimethyl-tetrahydro-cyclopenta-[1,3] dioxol-5-ol (**5**) (0.41 g, 1.0 mmol)[30] **11** (0.28 g, 88%) was obtained; mp 92-94 °C; $[\alpha]_D^{20}$ -15.9 (*c* 1.1, $CHCl_3$); IR (KBr): 3492*m*, 2933*s*, 2859*m*, 1654*w*, 1560*w*, 1473*m*, 1378*s*, 1260*s*, 1213*s*, 1143*s*, 1060*s*, 1000*s*; $^1$H-NMR (250 MHz, $CDCl_3$): 0.10 (*s*, 6 H, $SiMe_2$); 0.90 (*s*, 6 H, $Me_3$ of *t*-Bu); 1.25 (*s*, 3 H, Me$^i$); 1.42 (*s*, 3 H, Me$^i$); 1.65 (*m*, 1 H); 2.60 (*bs*, 2 H, exchangeable with $D_2O$, HO-C(4a, 5)); 3.63 (*dd*, *J* = 5.4, 8.5 Hz, 1 H); 3.70-4.10 (*m*, 1 H); 3.34 (*t*, *J* = 5.7 Hz, 1 H); 4.56 (*t*, *J* = 5.8 Hz, 1 H); $^{13}$C-NMR (62 MHz, $CDCl_3$): -4.56 (*q*, $Me_2Si$); 18.33 (*s*, $C_q$ of *t*-Bu); 23.82 (*q*, Me$^i$); 25.76 (*q*, Me$^i$); 25.86 (*q*, 3 x Me of *t*-Bu); 44.92 (*d*, C(4)); 60.65 (*t*, C(5)); 75.00, 77.14, 77.53, 78.58 (each *d*, C(1,2,3,4a)); 110.31 (*s*, $C_q^i$); MS (ei, 80 eV, 62°): 303 (3.8), 262 (2.5), 261 (14.4), 203 (43.5), 185 (33.6), 161 (19.9), 157 (20.4), 155 (10.2), 129 (35.8), 117 (18.7), 111 (11.6); Anal. calcd. for $C_{15}H_{30}SiO_5$ (318.49): C, 56.57; H, 9.49; found: C, 56.88; H, 9.22.

**3-*O*-*p*-Bromobenzyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose** (**15**).- To a solution of **18** (1.0 g, 3.84 mmol) in anhydrous THF (7 *ml*) sodium hydride (0.102 g, 4.23 mmol, 1.1 equiv.) was added in several portions under vigorous stirring at 5 °C for 15 min. The mixture was allowed to warm to room temperature, stirred for another 15 min and *p*-bromobenzyl bromide (1.0 g, 4.0 mmol, 1.05 equiv.) and a catalytic amount of tetra-*n*-butyl ammonium iodide (15 mg) were added. After stirring for 1 h the reaction was quenched by the addition of a saturated solution of ammonium chloride (10 *ml*), the mixture was extracted with diethyl ether (3 x 75 *ml*), the organic phase was washed with brine (5 *ml*) and dried ($MgSO_4$), and the solvent was evaporated. The residue was subjected to column chromatography (silica gel, hexanes/ethyl acetate 20:1 → 10:1) and **15** (1.24 g, 86%) was obtained as an oil; $[\alpha]_D^{20}$ -27.4 (*c* 1.1, $CHCl_3$); $R_F$ = 0.92 (hexanes/ethyl acetate 1:1); IR (film): 2986*s*, 2935*s*, 2892*m*, 1898*w*, 1734*w*, 1653*w*, 1594*w*, 1489*s*, 1456*m*, 1410*m*, 1382*s*, 1372*s*, 1348*m*, 1302*m*, 1254*s*, 1216*s*, 1165*s*, 1123*s*, 1071*s*, 1013*s*; $^1$H-NMR (250 MHz, $CDCl_3$): 1.31, 1.36, 1.42, 1.49 (each *s*, 3 H, 4 x Me); 3.96-4.02 (*m*, 2 H, $H_{A,B}$-C(6)); 4.08-4.14 (*m*, 2 H, H-C(3, 4)); 4.33 (*ddd*, *J* = 5.8, 6.0, 8.0 Hz, 1 H, H-C(5)); 4.57 (*d*, *J* = 3.7 Hz, 1 H, H-C(2)); 4.57 and 4.65 (*AB*, *J* = 12.0 Hz, $CH_2$-aryl); 5.89 (*d*, *J* = 3.7 Hz, 1 H, H-C(1)); 7.22 (*d*, *J* = 8.4 Hz, 2 H, H-C(2′, 6′)); 7.46 (*d*, *J* = 8.4 Hz, 2 H, H-C(3′, 5′)); $^{13}$C-NMR (75 MHz, $CDCl_3$): 25.41, 26.21, 26.78, 26.79 (each *q*, 4 x Me); 67.43 (*t*, C(6)); 71.48 $CH_2$-aryl); 72.29 (*d*, C(5)); 81.18, 81.67, 82.52 (each *d*, C(2, 3, 4)); 105.13 (*d*, C(1)); 108.90 and 111.68 (each *s*, $C_q$ of isopropylidene); 121.53 (*s*, C(4′)); 129.07 (*d*, C(2′, 6′)); 131.32 (*d*, C(3′, 5′)); 136.47 (*s*, C(1′)); MS (ei, 80 eV, 135°): 430 (0.25), 429 (0.34), 428 (0.28), 427 (0.36), 415 (4.0), 413 (3.8), 372 (5.6), 370 (6.0), 357 (2.1), 355 (2.4), 314 (1.4), 312 (1.5), 169 (91.9), 171 (89.6); Anal. calcd. for $C_{19}H_{25}BrO_6$ (429.31): C, 53.16; H, 5.87; found: C, 53.29; H, 6.01.

**3-*O*-*p*-Cyanobenzyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose** (**16**).- According to the preparation of **15** from **18** (1.0 g, 3.84 mmol) and *p*-bromomethylbenzonitrile (0.784 g, 4.0

mmol) **16** (1.35 g, 88%) was obtained as an oil; $[\alpha]_D^{20}$ -39.0 (*c* 1.4, $CHCl_3$); $R_F$ = 0.82 (hexanes/ethyl acetate 1:1); IR (film): 2987*s*, 2935*s*, 2894*s*, 2360*w*, 2229*s*, 1928*w*, 1737*w*, 1611*m*, 1574*w*, 1509*m*, 1456*m*, 1417*m*, 1372*s*, 1292*m*, 1255*s*, 1216*s*, 1165*s*, 1127*s*, 1077*s*, 1021*s*; $^1$H-NMR (300 MHz, $CDCl_3$): 1.32, 1.36, 1.42, 1.50 (each *s*, 3 H, 4 x Me); 3.98-4.03 (*m*, 2 H, $H_{A,B}$-C(6)); 4.09-4.16 (*m*, 2 H, H-C(3,4)); 4.35 (*ddd*, *J* = 5.6, 5.8, 8.5 Hz, 1 H, H-C(5)); 4.61 (*d*, *J* = 3.7 Hz, 1 H, H-C(2)); 4.70 and 4.77 (*AB*, *J* = 13.0 Hz, $CH_2$-aryl); 5.91 (*d*, *J* = 3.7 Hz, 1 H, H-C(1)); 7.47 (*d*, *J* = 8.4 Hz, 2 H, H-C(2′,6′)); 7.64 (*d*, *J* = 8.4 Hz, 2 H, H-(C3′, 5′)); $^{13}$C-NMR (75 MHz, $CDCl_3$): 25.41, 26.20, 26.77, 26.82 (each *q*, 4 x Me); 67.54 (*t*, C(6)); 71.19 (*t*, $CH_2$-aryl); 72.18 (*d*, C(5)); 81.15, 82.13, 82.43 (each *d*, C(2,3,4)); 105.12 (*d*, C(1)); 109.03, 111.79 (each *s*, $C_q$ of isopropylidene); 111.39 (*s*, C(4′)); 118.53 (*s*, CN); 127.53 (*d*, C(2′, 6′)); 132.00 (*d*, C(3′, 5′)); 142.98 (*s*, C(1′)); MS (ei, 80 eV, 139°): 375 (0.2), 361 (3.8), 360 (15.9), 302 (3.6), 174 (3.6); Anal. calcd. for $C_{20}H_{25}NO_6$ (375.43): C, 63.99; H, 6.71; N, 3.73; found: C, 63.90; H, 6.77; N, 3.49.

**1,2:5,6-Di-*O*-isopropylidene-3-*O*-(2-naphthylmethyl)-α-D-glucofuranose (17)**

According to the preparation of **15** from **18** (1.0 g, 3.84 mmol) and 2-bromomethyl-naphthaline (0.884 g, 4.0 mmol) **17** (1.18 g, 88%) was obtained as an oil; $[\alpha]_D^{20}$ -29.4 (*c* 1.5, $CHCl_3$); $R_F$ = 0.91 (hexanes/ethyl acetate 1:1); IR (film): 3055*w*, 2986*s*, 2934*s*, 2892*m*, 1920*w*, 1708*w*, 1634*w*, 1603*w*, 1510*m*, 1455*m*, 1381*s*, 1372*s*, 1339*m*, 1256*s*, 1215*s*, 1165*s*, 1125*s*, 1073*s*, 1025*s*; $^1$H-NMR (250 MHz, $CDCl_3$): 1.30, 1.39, 1.43, 1.48 (each *s*, 3 H, 4 x Me); 4.00-4.18 (*m*, 4 H, H-C(3,4,$6_A$,$6_B$)); 4.42 (*ddd*, *J* = 6.0, 6.1, 7.8 Hz, 1 H, H-C(5)); 4.62 (*d*, *J* = 3.7 Hz, 1 H, H-C(2)); 4.77 and 4.84 (*AB*, *J* = 12.1 Hz, $CH_2$-aryl); 5.92 (*d*, *J* = 3.7 Hz, 1 H, H-C(1)); 7.44-7.50 (*m*, 3 H, aryl); 7.79-7.82 (*m*, 4 H, aryl); $^{13}$C-NMR (62 MHz, $CDCl_3$): 25.47, 26.26, 26.80, 26.83 (each *q*, 4 x Me); 67.44 (*t*, C(6)); 72.42 (*t*, $CH_2$-aryl); 72.54 (*d*, C(5)); 81.38, 81.65, 82.71 (each *d*, C(2, 3, 4)); 105.34 (*d*, C(1)); 109.01 and 111.80 (each *s*, $C_q$ of isopropylidene); 125.64, 125.98, 126.16, 126.44, 127.69, 127.87, 128.19 (each *d*, aryl); 133.07, 133.25, 135.10 (each *s*. $C_q$ of aryl); MS (ei, 80 eV, 132°): 400 (4.7), 385 (1.4), 342 (5.6), 284 (1.4), 199 (1.3), 183 (1.4), 101(27.4); Anal. calcd. for $C_{23}H_{28}O_6$ (400.48): C, 68.98; H, 7.05; found: C, 69.05; H, 7.09.

**1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (18)**

a) From **14**: [33] From **14** (0.35 g, 1.0 mmol, prepared in 87.3% yield from **18** following the procedure given by *Czernecki et al.*[34]) **18** (0.22 g, 86%) was obtained: mp 110-112 °C, $[\alpha]_D^{20}$ -13.3 (*c* 1, $CHCl_3$) (Lit.:[35, 36] mp 110-112 °C, $[\alpha]_D^{20}$ -13.5 ($CHCl_3$)).

b) From **15**: From **15** (0.43 g, mmol) **18** (0.22 g, 85%) was obtained: mp 109-111 °C, $[\alpha]_D^{20}$ -13.0 (*c* 1, $CHCl_3$).

c) From **16**: From **16** (0.38 g, 1.0 mmol) **18** (0.23 g, 87%) was obtained: mp 110-112 °C, $[\alpha]_D^{20}$ -13.2 (*c* 1, $CHCl_3$).

d) From **17**: From **17** (0.40 g, 1.0 mmol) **18** (0.24 g, 90%) was obtained: mp 109-111 °C, $[\alpha]_D^{20}$ -13.1 (*c* 1, $CHCl_3$).

**Benzyl β-D-galactopyranoside (13).**- From benzyl 3,4-O-isopropylidene-β-D-galactopyranoside (**12** ) (0.24 g, 1.0 mmol)[33] **13** (0.24 g, 90%) was obtained: mp 116-118 °C, $[\alpha]_D^{20}$ -24.7 (*c* 1, $CHCl_3$) (Lit.:[33] mp 117-118°, $[\alpha]_D^{20}$ -25.3 (*c* 2.6, $CHCl_3$).

**Acknowledgment.**- Financial support by the European Communities (SC1*-CT92-0780) and the Fonds der Chemischen Industrie is gratefully acknowledged; we are indebted to *Prof. Dr. R. Neidlein*, Pharmazeutisch-Chemisches Institut, Universität Heidelberg, for his encouragement, to *Dr. P. Rosyk* for his help with the manuscript and to Perkin-Elmer Ltd. for support.

## REFERENCES AND NOTES


1 Greene, T. W.; Wuts, P. G. M. "*Protective Groups in Organic Chemistry*", 2nd ed., Wiley, New York, 1991.
2 Heathcock, C. H.; Ratcliffe, R. *J. Am. Chem. Soc.* **1971**, *93*, 1746.
3 Hartung, W. H.; Simonoff, C. *Org. React.* **1953**, *7*, 263.
4 Hanessian, S.; Liak, T. J.; Vanasse, B. *Synthesis* **1981**, 396.
5 Horita, K.; Yoshioka, T.; Tanaka, T.; Oikawa, Y.; Yonemitsu, O. *Tetrahedron* **1986**, *42*, 3021.
6 Oikawa, Y.; Tanaka, T.; Yonemitsu, O. *Tetrahedron Lett.* **1986**, *27*, 3647.
7 Schön, I. *Chem. Rev.* **1984**, *84*, 287.
8 Mairanovsky, V. G. *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 281.
9 Anantharamaiah, G. M.; Sivanandiah, K. M. *J. Chem. Soc, Perkin Trans 1* **1977**, 490.
10 Guindon, Y.; Yoakim, C.; Morton, H. E. *Tetrahedron Lett.* **1983**, *24*, 2969.
11 Vankar, Y. D.; Rao, C. T. *J. Chem. Res. Synop.* **1985**, 232.
12 Williams, D. R.; Brown, D. L.; Benbow, J. W. *J. Am. Chem. Soc.* **1989**, *111*, 1923.
13 Hori, H.; Nisihida, Y.; Ohrui, H.; Meguro, H. *J. Org. Chem.* **1989**, *54*, 1346.
14 Kartha, K. P. R.; Dasgupta, F.; Singh, P. P.; Srivastava, H. C. *J. Carbohydr. Chem.* **1986**, *5*, 437.
15 THoye, T. R.; Caruso, A. J.; Dellaria Jr., J. F.; Kurth, M. J. *J. Am. Chem. Soc.* **1982**, *104*, 6704.
16 Holland, H. L.; Conn, M.; Chenchaiah, P. C.; Brown, F. M. *Tetrahedron Lett.* **1988**, *29*, 6393.
17 Kawana, M. *Chem. Lett.* **1981**, 1541.
18 Angyal, S. J.; James, K. *Carbohydr. Res.* **1970**, *12*, 147.
19 Sihuda, P. F.; Cichowicz, M. B.; Heimann, M. R. *Tetrahedron Lett.* **1983**, *24*, 3829.
20 Angibeaud, P.; Defaye, J.; Gadelle, A.; Utille, J.-P.*Synthesis* **1985**, 1123.
21 Schmidt, W.; Steckhan, E. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 801.
22 Curci, R.; D´Accolti, L.; Detomaso, A.; Fusco, C.; Takeuchi, K.; Ohga, Y.; Eaton, P. E.; Yip, Y. C. *Tetrahedron Lett.* **1993**, *34*, 4559.
23 Similiarly, from (4a *R*)-5-*O*-benzyl-4a-carba-4,4a-hydroxy-2,3-*O*-isopropylidene-1-*O*-methyldiphenylsilyl-α-D-ribofuranose (**9**) under the same conditions a 87% yield of (4a *S*)-4a-carba-4,4a-dihydroxy-2,3-*O*-isopropylidene-1-*O*-methyldiphenylsilyl-α-D-ribofuranose (**10**) was obtained.[30]
24 Marples, B. A.; Muxworthy, J. P.; Baggaley, K. H. *Synlett* **1992**, 646.
25 Halcomb, R. L.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 6661.
26 From the effects of steric hinderance on the retardation of the debenzylation it [24] was concluded that the reaction proceeds rather *via* a butterfly polar transition state [38] than *via* a free radical mechanism. [39]
27 Adam, W.; Hadjiarapoglou, L.; A. Smerz, A. *Chem. Ber.* **1991**, *124*, 227.
28 Hudlicky, M. *J. Org. Chem.* **1980**, *45*, 5377.
29 This condenser was taken from a Macro Diazald Kit manufactured by Aldrich Co.
30 The synthesis of this compound will be reported elsewhere (Csuk, R.; Dörr, P. unpublished results, 1994).
31 Marquez, V. E.; Lim, M.-I.; Tseng, C. K.-H.; Markovac, A.; Priest, M. A.; Khan, M. S.; Kaskar, B. *J. Org. Chem.* **1988**, *53*, 5709.
32 Ogura, H.; Takahashi, H.; Itoh, T. *J. Org. Chem.* **1972**, *37*. 72.
33 Collins, P. M. "Carbohydrates", Chapman and Hall Ltd, London 1987.
34 Czernecki, S.; Georgoulis, C.; Provelenghiou, C. *Tetrahedron Lett.* **1976**, 39, 3535.
35 Fischer, E.; Rund, C. *Ber. Deutsch. Chem. Ges.* **1916**, *49*, 88.
36 Ohle, H.; v. Vargha, L. *Ber. Deutsch. Chem. Ges.* **1929**, *62*, 2425.
37 Klemer, A.; Hofmeister, U.; Lemmes, R. *Carbohydr. Res.* **1979**, *68*, 391.
38 Marples, B. A.; Muxworthy, J. P.; Baggaley, K. H. *Tetrahedron Lett.* **1991**, *32*, 533.
39 Baumstark, A. L.; Beeson, M.; Vasquez, P. C. *Tetrahedron Lett.* **1989**, *30*, 5567.
40 Weidmann, H. *Monatsh. Chem.* **1965**, *96*, 766.


(*Received in Germany* 16 *May* 1994; *accepted* 24 *June* 1994)