group.[14] The filtrate was chromatographed on silica gel. Eluting with hexane gave the arylamine followed by 20% ether–hexane to obtain diphenyl disulfide. The results are shown in Table II.

Photolysis of Solid *N*-Phenylbenzenesulfonamide. *N*-Phenylbenzenesulfonamide (0.5 g) in finely powdered state was irradiated for 20 h. During which it acquired a pale brown color. TLC analysis of the photolysate revealed the presence of anilinium benzenesulfonate (R_f 0.86), aniline (R_f 0.65), and diphenyl disulfide (R_f 0.37) together with a large proportion of brown resinous material of unknown structure.

Crossover Photolysis. A solution of *N*-*p*-tolylbenzenesulfonamide (0.5 g) and *N*-phenyl-*p*-toluenesulfonamide (0.5 g) in 2-propanol (100 mL) was irradiated for 15 h. The solid obtained, namely, the arylammonium sulfonate salt, was analyzed by TLC and mixture melting point and found to contain the crossbred *p*-toluidinium *p*-toluenesulfonate salt (mp and mmp 197–199 °C) together with the expected arylamine salts: *p*-toluidinium benzenesulfonate (mp and mmp 205 °C) and anilinium *p*-toluenesulfonate, mp and mmp 228–230 °C.

Preparation of Reference Compounds. *N*-Phenylbenzenesulfonamide:[15] crystallized from ethanol, mp 111–112 °C. *N*-*p*-Tolylbenzenesulfonamide:[15] crystallized from ethanol, mp 120–121 °C. Carbazole:[16] crystallized from benzene, mp 245–246 °C; picrate, mp 185–186 °C. 3-Methylcarbazole:[17] crystallized from ethanol, mp 209 °C; picrate mp 179 °C. 3,6-Dimethylcarbazole:[17] crystallized from ethanol, mp 219–221 °C; picrate, mp 194–195 °C. *o*-Aminophenyl phenyl sulfone:[18] crystallized from ethanol, mp 176 °C. *p*-Aminophenyl phenyl sulfone:[18] crystallized from ethanol, mp 122 °C. *o*-Aminobiphenyl:[19] crystallized from petroleum ether (bp 40–60 °C), mp 49–50 °C; acetyl derivative, mp 121 °C. *p*-Aminobiphenyl:[19] crystallized from petroleum ether (bp 40–60 °C), mp 51–52 °C; acetyl derivative, mp 171 °C. 2-Amino-5-methylbiphenyl:[20] viscous oil; bp 135–140 °C (3 mmHg); chloroacetyl derivative, mp 89 °C. 1-Phenylisoquinoline:[21] crystallized from benzene/petroleum ether (bp 60–80 °C) mmp 94–95 °C; picrate, mp 165 °C. Phenyl *m*-tolyl sulfone:[22] crystallized from ethanol, mp 125–126 °C. 3-Methylphenothiazine 5,5-dioxide:[24] sublimed, mp 283–284 °C.

Registry No. *N*-Phenylbenzenesulfonamide, 1678-25-7; *N*-(*p*-tolyl)benzenesulfonamide, 6311-65-5.

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Reduction of 1-*O*-Acyl-α-D-glucopyranoses to α-Glucosides and to 1,5-Anhydroglucitol

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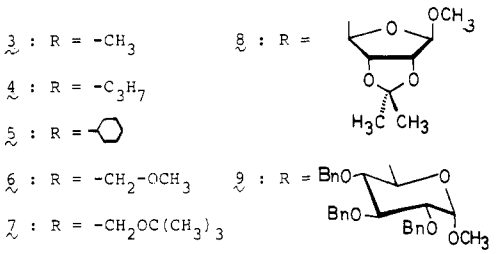
Received April 2, 1981

The convenient synthesis of 1-*O*-acyl-2,3,4,6-tetra-*O*-benzyl-α-D-glycopyranoses was viewed as a starting point for preparation of α-glycosides of primary alcohols by way of diborane reduction of the ester function (Scheme I, path A.[2] However, under the reaction conditions used for the reduction of esters[2] acetals are also cleaved to ethers[3] (path B). Therefore, 1-*O*-acylglycoses, structural analogues of half-acylals (1), may be attacked by reducing agents at two positions (A and B). A competitive reaction observed during the reduction of esters to ethers leads to hydrolytic cleavage of the ester bond.[2e,4]

The utility of the diborane reduction method for either the glycoside (path A) or the anhydroalditol (path B) synthesis was investigated by starting from 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (**2**).[5] Compound **2** was acylated with different acid chlorides[6,7] in the presence of pyridine at 0 °C. 1-*O*-Acyl-α-D-glucopyranoses **3α–9α**,[8] with minor amounts of β derivatives (**3β–9β**), were obtained in high yields (Table I).

Model reductions with **3** (α/β mixture) under different reaction conditions (varying solvent, reducting agent, Lewis acid, and molar ratio[1]) showed that the best results were obtained with **3**, sodium borohydride, and boron trifluoride etherate (molar ratio 1:4:37) with diglyme as the solvent (see the Experimental Section and Table II). Only α-glucosides were obtained as verified by an independent synthesis of **3A**.[9] The reaction conditions given for the reduction of esters to ethers[2b] led to incomplete reduction of **3**.

Table II indicates that the common acyl derivatives **3α–5α** were reduced to the α-glycosides **3A–5A** in good yields. Only minor cleavage of the ester bond was observed chromatographically, resulting in the formation of small amounts of **2** (less than 10% as byproduct[4] (Scheme II). However, introduction of α-alkoxy substituents in the acyl group (**6α, 7α**) led to preferred acetal cleavage in producing



10 and diminished ester reduction to **6A** and **7A**. This phenomenon is attributed to a different intramolecuar

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(4) Hydrolytic cleavage is perhaps due to the presence of traces of water or to intermediate formation of a glycosyl fluoride whichis hydrolyzed during workup.
(5) Compound **2** was obtained according to a procedure by P. J. Glaudemans and H. J. Fletcher in "Methods in Carbohydrate Chemistry", Vol. 6, R. L. Whistler and J. N. Bemiller, Eds., Academic Press, New York, 1972, p 374.
(6) Methyl 2,3-*O*-isopropylidene-β-D-ribofuranuronosyl chloride was obtained according to a procedure by R. R. Schmidt, K. H. Jung, and P. Hermentin, *Chem. Ber.*, 111, 3311 (1978).
(7) Methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranuronosyl chloride was obtained according to a procedure by P. Kovac, *Carbohydr. Res.*, **31**, 326 (1973); R. R. Schmidt and E. Rücker, *Tetrahedron Lett.*, **21**, 1421 (1980); E. Rücker, Thesis, Universität Konstanz, 1980.
(8) Compound **3** was obtained according to a procedure byR. U. Lemieux, K. B. Hendriks, R. v. Stick, and K. James, *J. Am. Chem. Soc.*, **97**, 4056 (1975).
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Table I. 1-O-Acyl-D-glucopyranoses 3α–9α and 3β–9β[a]

compd	yield,[b] %	ratio of α/β	mp, °C	^{1}H NMR data[c] H-1[d]	H-2[d]	$J_{1,2}$, Hz	IR data ν_{CO}, cm^{-1}	R_f[e] A	B
3α	f	10:1	oil	6.38 (3)	g	3.0	1750	0.56	0.61
3β			oil	5.65 (d)	g	7.0	1750	0.54	0.61
4α	85	10:1	oil	6.42 (d)	3.77	3.0	1740	0.62	0.84
4β			oil	5.55 (d)	g	7.2	1740	0.59	0.84
5α	96	10:1	oil	6.42 (d)	3.82	3.0	1740	0.67	0.79
5β			oil	5.65 (d)	g	7.2	1740	0.62	0.79
6α	92	10:1	oil	6.35 (d)	g	3.0	1760	0.48	0.47
6β			oil	5.62 (d)	g	7.2	1760	0.40	0.47
7α[j]	95	6:1	oil	6.33 (d)	g	3.1	1770	0.42	0.66
7β[j]			87–88	5.62 (d)	g	7.1	1770	0.38	0.66
8α[h]	98	19:1	oil	6.49 (d)	g	3.2	1768	0.51	0.68
8β			oil	5.67 (d)	g	7.0	1774	0.42	0.62
9α[i]	41	5:1	oil	6.36 (d)	3.85	2.8	1760	0.69	0.57
9β			98–99	5.63 (d)	g	6.8	1760	0.58	0.52

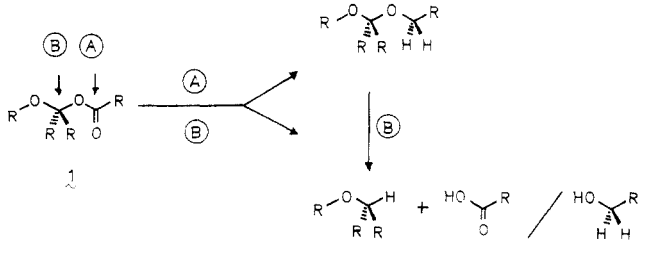
[a] All compounds gave correct elemental analyses. [b] Isolated yields. [c] 80-MHz spectra in $CDCl_3$ with internal Me_4Si. [d] δ values. [e] TLC on silical gel: eluant A, $CHCl_3$/ether (20:1); eluant B, petroleum ether (bp 40–60 °C)/ether (1:1). [f] See ref 8. [g] The values could not be obtained from the 80-MHz ^{1}H NMR spectrum. [h] See ref 6. [i] See ref 7. [j] Reaction of 2 with *tert*-butoxyacetic acid and dicyclohexylcarbodiimide.

Table II. Alkyl α-D-Glucopyranosides 3A–7A by Reduction[a]

starting matl	reaction time,[b] h	eluant[b] ratio, $CHCl_3$/ether	products (yield,[c] %; R_f[d]
3α	6	15:1	**3A** (64; 0.67, 0.72)[e]
4α	20	20:1	**4A** (61; 0.71, 0.81)
5α	12	20:1	**5A** (61; 0.74, 0.84)
6α	72	10:1	**6A** (13; 0.34, 0.35), **10** (47; 0.57, 0.65)
6α[f]	72	10:1	**6A**-d_2 (13; 0.34, 0.35), **11** (53; 0.57, 0.65)
7α	72	g	**7A**[h] (6; 0.43, 0.44), **10** (40; 0.57, 0.65)

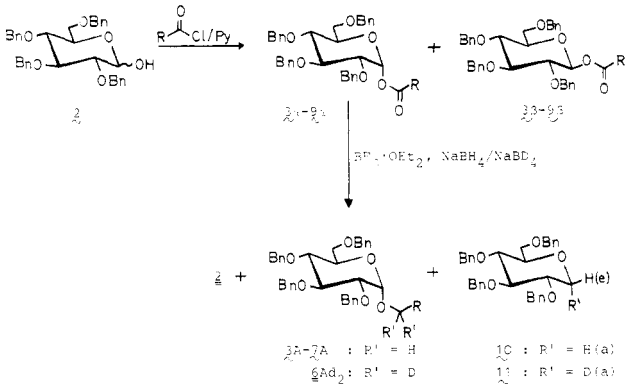
[a] All compounds gave correct elemental analyses. [b] See the Experimental Section. [c] Isolated yields. [d] TLC on silica gel with $CHCl_3$/ether (20:1) and petroleum ether (bp 40–60 °C)/ether (1:1). [e] Identical with material received independently; see ref 8. [f] Reduction with $NaBD_4$. [g] Eluant: chloroform/petroleum ether (bp 40–60 °C)/ether (12:12:1). [h] Identified only by ^{1}H NMR.

Scheme I



complexation of the Lewis acid with the ester and to the inductive effect of the α-alkoxy substituent. With 8α and 9α, disaccharides **8A** and **9A** were not obtained; slow reaction led to **10** and **2** as the main products.[1] The additional acetal groups in **8** and **9** are less reactive; they were therefore not affected under the applied reaction conditions. Reduction of 6α with $NaBD_4$ led to **6A**-d_2 and, with

Scheme II



retention of configuration at the anomeric center, to the 1,5-anhydroglucitol **11**: ^{1}H NMR ($CDCl_3$, internal Me_4Si) for **10** δ 4.0 [H-1 (e), J_{gem} = 10 Hz, $J_{1,2}$ = 3.5 Hz], δ 3.15 [H-1 (a), $J_{gem} = J_{1,2}$ = 10 Hz]; for **11**, δ 3.95 [H-1 for (e), $J_{1,2}$ 3.5 Hz], H-1 (a), signal not observed.

Experimental Section

The general procedure for the reduction was as follows. To 3α–7α (0.86 mmol) and $NaBH_4$ (130 mg, 3.42 mmol) in 10 mL anhydrous diglyme was added boron trifluoride etherate (4 mL, 31.6 mmol) within 20 min at 0 °C (nitrogen atmosphere). After the mixture was kept for 1 h at 0 °C, the reaction was continued at room temperature for several hours (Table II). The reaction was stopped by the addition of water (20 mL). The product was extracted with ether (200 mL), and the extract was washed with water to neutrality, dried (anhydrous sodium sulfate), and evaporated to dryness. The product was chromatographed on silica gel (for eluants and yields see Table II).

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Registry No. 2, 38768-81-9; 3α, 56822-49-2; 3β, 56822-48-1; **3A**, 78890-53-6; 4α, 78890-54-7; 4β, 78890-55-8; **4A**, 78890-56-9; 5α, 78890-57-0; 5β, 78890-58-1; **5A**, 74741-49-4; 6α, 78890-59-2; 6β, 78890-60-5; **6A**, 78890-61-6; **6A**-d_2, 78890-70-7; 7α, 78890-62-7; 7β, 78890-63-8; **7A**, 78890-64-9; 8α, 78890-65-0; 8β, 74808-15-4; 9α, 78890-66-1; 9β, 78890-67-2; **10**, 78890-68-3; 11, 78890-69-4; acetyl chloride, 75-36-5; butanoyl chloride, 141-75-3; cyclohexanoyl chloride, 2719-27-9; methoxyacetyl chloride, 38870-89-2; *tert*-butoxyacetyl chloride, 78826-46-7; 2,3-isopropylidene-β-D-ribofuranuronoyl chloride, 68673-82-5; 1-methyl-2,3,4-tribenzyl-2-D-glucopyranuronoyl chloride, 78890-71-8.