Carbohydrate Research, 232 (1992) 359–365
Elsevier Science Publishers B.V., Amsterdam

Note

An improved preparation of 2,3,5-tri-*O*-acyl-β-D-ribofuranosyl azides by the Lewis acid-catalysed reaction of β-D-ribofuranosyl acetates and trimethylsilyl azide: an example of concomitant formation of the α anomer by trimethylsilyl triflate catalysis

Anton Štimac [a] and Jože Kobe [b]

[a] *Krka, Pharmaceutical and Chemical Works, C. herojev 45, 68000 Novo mesto (Slovenia)*
[b] *Boris Kidrič Institute of Chemistry, Hajdrihova 19, 61115 Ljubljana (Slovenia)*

(Received November 14th, 1991; accepted January 30th, 1992)

An improved synthesis [1] of 2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl azide (**3**) involves the reaction of trimethylsilyl azide in the presence of a Lewis acid with 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose [2–4] (**1**) rather than the action of sodium azide upon the corresponding halide [5]. Titanium tetrachloride, aluminum chloride, and boron trifluoride etherate were suggested [2] to be catalysts that are as equally effective as trimethylsilyl trifluoromethanesulfonate [3] (triflate) and stannic chloride [4,6]. 2,3,5-Tri-*O*-acyl-β-D-ribofuranosyl azides were formed exclusively from the corresponding glycosyl acetates [2–6]. However, excessive proportions of either trimethylsilyl azide and/or the catalyst were employed in most of these reactions, which is not only wasteful but makes the isolation step more difficult.

We now report that the preparation of **3** can be simplified by using a 10% excess of trimethylsilyl azide and 0.05 mol equiv of catalyst. Dichloromethane was selected as a reaction medium owing to its favourable solvent effect [2]. With stannic chloride as the catalyst, the rate of reaction was almost independent of the concentration above 0.03 mol equiv, and the use of 0.05 mol equiv was more effective than 0.1 mol equiv of titanium tetrachloride, trimethylsilyl triflate, aluminum chloride, boron trifluoride etherate, and magnesium bromide etherate in promoting the reaction of **1** with trimethylsilyl azide to give **3** (Figs. 1 and 2). With stannic chloride, there was a 99.4% conversion within 4 h (cf. 96% with titanium tetrachloride in 30 h and 99.6% with trimethylsilyl triflate in 9 days). Boron trifluoride etherate, magnesium bromide etherate, and aluminum chloride were

Correspondence to: Dr. J. Kobe, Boris Kidrič Institute of Chemistry, Hajdrihova 19, 61115 Ljubljana, Slovenia.

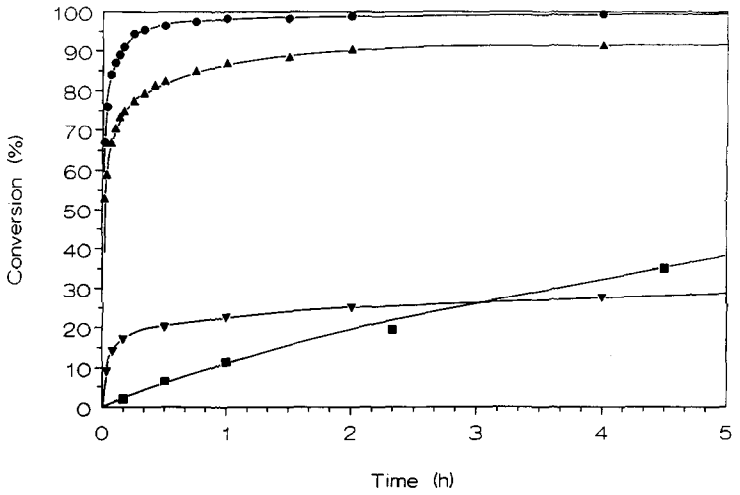


Fig. 1. The conversion **1** → **3** with trimethylsilyl azide (1.1 mol equiv) in dichloromethane at room temperature, catalysed by 0.05 mol equiv of stannic chloride (●), and 0.1 mol equiv of titanium tetrachloride (▲), boron trifluoride etherate (▼), and trimethylsilyl triflate (■).

unsatisfactory at 0.1 mol equiv. Each catalyst, except trimethylsilyl triflate, gave the β-azide **3** exclusively, following the general principle [1] of the formation of 1,2-*trans* products. However, trimethylsilyl triflate gave a 3:17 α,β-mixture (**3** + **5**) that was resolved by HPLC. The structure of the α anomer **5** was indicated by the analytical

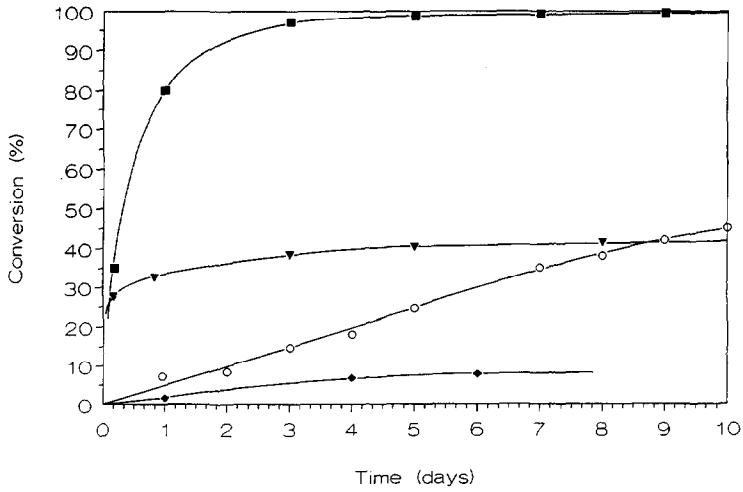
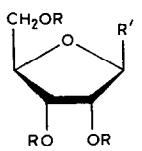
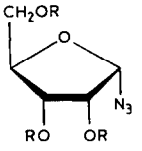


Fig. 2. The conversion **1** → **3** with trimethylsilyl azide (1.1 mol equiv) in dichloromethane at room temperature in the presence of 0.1 mol equiv of trimethylsilyl triflate (■), boron trifluoride etherate (▼), and magnesium bromide etherate (◆), and the anomerisation **5** → **3** by stannic chloride (0.1 mol equiv) under the same conditions (○).

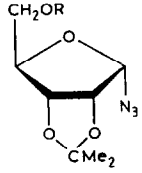
and ^{1}H-NMR data. The $J_{1,2}$ value (5.1 Hz) and the chemical shift of the H-1 resonance (5.90 ppm, 0.27 ppm downfield of the H-1 resonance of **3**) are characteristic of α-ribofuranosides [7]. The $\alpha \rightarrow \beta$ transformation (**5** → **3**) occurred slowly on treatment of **5** with stannic chloride in the presence or absence of trimethylsilyl azide (Fig. 2). *O*-Debenzoylation of **5** gave α-D-ribofuranosyl azide (**6**), isopropylidenation of which yielded known [2] 2,3-*O*-isopropylidene-α-D-ribofuranosyl azide (**7**). Since the $[\alpha]_D$ value [+57° ($CHCl_3$)] was almost the opposite of that (−55.8°) reported [2], another means for the unambiguous preparation of **7** was sought.



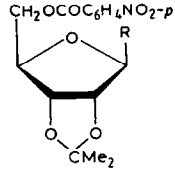
1 R = Bz, R' = OAc
2 R = Ac, R' = OAc
3 R = Bz, R' = N_3
4 R = Ac, R' = N_3



5 R = Bz
6 R = H



7 R = H
10 R = $COC_6H_4NO_2$-*p*



8 R = Br
9 R = N_3

Treatment of 2,3-*O*-isopropylidene-5-*O*-(*p*-nitrobenzoyl)-β-D-ribofuranosyl bromide [8] (**8**) with sodium azide in hexamethylphosphoric triamide gave 2,3-*O*-isopropylidene-5-*O*-(*p*-nitrobenzoyl)-α-D-ribofuranosyl azide (**10**) together with the β anomer **9** in the ratio 17:3 (^{1}H-NMR data). Similar to earlier observations [2], the α anomer **10** was characterised by the signal for H-1 at δ 5.13 (d, $J_{1,2}$ 4.2 Hz) and an $[\alpha]_D$ value of +11.5° ($CHCl_3$) and the β anomer **9** by the signal for H-1 at δ 5.62 (s) and the $[\alpha]_D$ value of −165°. Compound **10** was *O*-deacylated (→ **7**) under basic conditions, and acid hydrolysis of **7** gave **6**, which was identical with the compound prepared from **5**. That **6**, not reported hitherto, exists in the furanoid form was established by ^{1}H-NMR spectroscopy of a solution in Me_2SO-d_6. One triplet and two doublets were present, corresponding to one primary and two secondary hydroxyl groups. Moreover, the physical data for **6** were different from those of the known isomeric β-D-ribofuranosyl [5a,c] and D-ribopyranosyl azides [9,10].

This significant decrease in selectivity when trimethylsilyl triflate was used as the catalyst was also observed with 1-*O*-acetyl-2-*O*-arylsulfenylribose derivatives [11]. Apparently, the increased hindrance on the top face of the system leads to lower selectivity, especially when the rate of addition of the azide is decreased due to the lower acidity of the trimethylsilyl triflate, which might modify the reaction mechanism [12].

EXPERIMENTAL

General procedures.—Dichloromethane was distilled from P_4O_{10} and stored over 4A molecular sieves. High-quality trimethylsilyl azide and the catalysts were

taken from freshly opened containers. Flash-column chromatography was carried out on Silica Gel 60 (Merck, 40–63 μm), and TLC and PLC on Silica Gel 60 F_{254} (Merck) with detection by UV light and/or by charring with H_2SO_4. Solvents were evaporated under diminished pressure at $< 40°$. Melting points are uncorrected. Optical rotations were measured with a Schmidt and Haensch polarimeter. The ^{1}H- (299.94 MHz, internal Me_4Si) and ^{13}C-NMR (75.43 MHz) spectra were recorded with a Varian VXR-300 instrument for solutions in $CDCl_3$ (δ 77.00), unless stated otherwise. The spectra were assigned by means of the corresponding $^{13}C-^1H$ chemical shift correlated spectra. IR spectra were recorded with a Bio-Rad FTS 15/18 spectrometer.

HPLC.—The course of the reaction of **1** (1-mmol scale) with Me_3SiN_3 in the presence of the various Lewis acids was monitored by HPLC, using a column (150 × 4.6 mm i.d.) of Lichrosorb Si 60 (5 μm) and elution with 1,2-dichloroethane at 1 mL/min. Samples (1 μL) were quenched by the addition of satd aq $NaHCO_3$ (1 drop), then extracted into the eluent (3 mL), and the extract was dried ($MgSO_4$), filtered through a 0.45-μm filter, and analysed by HPLC. The components were detected by a UV monitor (Knauer) at 254 nm. Retention times critically depended on the moisture present, but values typical for the solvent system, prepared by mixing dry 1,2-dichloroethane and satd aq 1,2-dichloroethane at 22°, in the ratio 5 : 1, were 4.8 min for **3**, 6.5 min for **5**, and 18.6 min for **1**. The rates of formation of products (**3** or **3** + **5**) are shown in Figs. 1 and 2.

2,3,5-Tri-O-benzoyl-β-D-ribofuranosyl azide (**3**).—To a solution of 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose [13] (**1**; 10.09 g, 20 mmol) and Me_3SiN_3 (2.9 mL, 22 mmol) in anhyd CH_2Cl_2 (40 mL) was added 50 mM $SnCl_4$ in CH_2Cl_2 (20 mL, 1 mmol). The mixture was stirred at room temperature for 12 h with the exclusion of moisture, satd aq $NaHCO_3$ (30 mL) was added, the aqueous phase was extracted with CH_2Cl_2 (30 mL), and the combined organic solutions were dried ($MgSO_4$) and concentrated to give **3** as a colorless oil (9.75 g, 100%; > 99% pure by HPLC). Crystallisation from MeOH afforded **3** with mp 66–67.5°, $[\alpha]_D^{25}$ −45° (*c* 3.11, $CHCl_3$) {lit. [5a] mp 66.5–67°, $[\alpha]_D^{22}$ −41.2° ($CHCl_3$); lit. [2] $[\alpha]_D^{25}$ −47.5° ($CHCl_3$)}; ν_{max}^{KBr} 2157 and 2113 (2 N_3, due to two crystalline forms [5a]), 1722 (C=O), 1603, 1450, 1374, 1266, 1245, 1119, 1068, 1025, 918, and 715 cm^{-1}. NMR data: ^{1}H, δ 4.56 (dd, 1 H, H-5a), 4.75–4.81 (m, 2 H, H-4,5b), 5.58 (dd, 1 H, H-2), 5.63 (d, 1 H, H-1), 5.85 (dd, 1 H, H-3), 7.31–7.62 (m, 9 H, Ar-H), 7.88–8.13 (3 m, each 2 H, Ar-H), $J_{1,2}$ 1.7, $J_{2,3}$ 4.9, $J_{3,4}$ 6.4, $J_{4,5a}$ 5.4, $J_{5a,5b}$ 13.3 Hz; ^{13}C, δ 63.73 (C-5), 71.45 (C-3), 75.27 (C-2), 79.82 (C-4), 93.28 (C-1), 128.42–129.78, and 133.23–133.68 (Ar–C), 165.03, 165.18, and 166.13 (3 C=O).

Trimethylsilyl triflate-catalysed reaction of **1** *with trimethylsilyl azide.*—To a solution of **1** (3.03 g, 6 mmol) and Me_3SiN_3 (0.88 mL, 6.6 mmol) in anhyd CH_2Cl_2 (6 mL) was added 50 mM $Me_3SiOSO_2CF_3$ in CH_2Cl_2 (12 mL, 0.6 mmol). The mixture was stirred at room temperature for 9 days in a tightly stoppered flask, then worked-up as described above, to give a mixture of **3** and 2,3,5-tri-*O*-benzoyl-α-D-ribofuranosyl azide (**5**) as a pale-yellow oil (2.9 g). The major part of **3** (1.63 g,

56%; mp 67.5–68°) was removed by crystallisation from MeOH. The residue, obtained after concentration of the mother liquor, was subjected to flash-column chromatography [1:1 1,2-dichloroethane–light petroleum (bp 40–70°) then 1,2-dichloroethane]. Unresolved fractions were rechromatographed by PLC with the former eluent, and the pure components were combined to give **3** (0.76 g, 26%) and **5** (0.33 g, 11%; > 99% pure by HPLC) as slightly yellow oils.

Compound **5** had R_3 0.8 (1,2-dichloroethane), $[\alpha]_D^{25}$ +104° (*c* 3.0, $CHCl_3$); ν_{max}^{KBr} 2116 (N_3), 1733 and 1723 (C=O), 1603, 1451, 1372, 1315, 1267, 1132, 1108, 1069, 1027, 941, 866, and 711 cm^{-1}. NMR data: ^1H, δ 4.60 (dd, 1 H, H-5a), 4.75 (dd, 1 H, H-5b), 4.81 (ddd, 1 H, H-4), 5.53 (dd, 1 H, H-2), 5.80 (dd, 1 H, H-3), 5.90 (d, 1 H, H-1), 7.30–7.62 (m, 9 H, Ar–H), 7.91–7.96 (m, 2 H, Ar–H), 8.05–8.11 (m, 4 H, Ar–H), $J_{1,2}$ 5.1, $J_{2,3}$ 6.5, $J_{3,4}$ 3.3, $J_{4,5a}$ 3.8, $J_{4,5b}$ 3.3, $J_{5a,5b}$ 12.1 Hz; ^{13}C, δ 63.75 (C-5), 70.81 (C-3), 71.86 (C-2), 81.30 (C-4), 90.07 (C-1), 128.44–129.88 and 133.36–133.61 (Ar–C), 165.15, 165.69, and 166.00 (3 C=O).

Anal. Calcd for $C_{26}H_{21}N_3O_7$ (487.47): C, 64.06; H, 4.34; N, 8.62. Found: C, 64.14; H, 4.36; N, 8.61.

Stannic chloride-promoted anomerisation of **5**.—To a solution of **5** (61 mg, 125 μmol) in anhyd CH_2Cl_2 (1 mL) was added 50 mM $SnCl_4$ in dichloromethane (0.5 mL, 25 μmol). The mixture was stirred at room temperature and the reaction was monitored by HPLC (see above). The rate of anomerisation within the first 10 days of reaction is shown in Fig. 2; 63% of **5** was converted into **3** after 27 days and 64% after 34 days.

*2,3,5-Tri-*O*-acetyl-β-*D*-ribofuranosyl azide* (**4**).—Prepared from 1,2,3,5-tetra-*O*-acetyl-β-D-ribofuranose [14] (**2**) by the procedure described for **3**, except that three re-extractions with CH_2Cl_2 were required, **4** (97%) had bp 75°/0.1 Pa, $[\alpha]_D^{25}$ −149° (*c* 1.0, $CHCl_3$) {lit. [6] $[\alpha]_D$ −116° ($CHCl_3$)}; ν_{max}^{film} 2116 (N_3), 1750 (C=O), 1435, 1374, 1232, 1094, 1066, 944, and 899 cm^{-1}. NMR data: ^1H, δ 2.08, 2.125, and 2.130 (3 s, each 3 H, 3 Ac), 4.15 (dd, 1 H, H-5a), 4.36 (ddd, 1 H, H-4), 4.42 (dd, 1 H, H-5b), 5.14 (dd, 1 H, H-2), 5.34 (dd, 1 H, H-3), 5.37 (d, 1 H, H-1), $J_{1,2}$ 2.0, $J_{2,3}$ 4.8, $J_{3,4}$ 6.7, $J_{4,5a}$ 4.1, $J_{4,5b}$ 3.2, $J_{5a,5b}$ 12.0 Hz; ^{13}C, δ 20.39, 20.44, and 20.61 (3 $OCOCH_3$), 62.93 (C-5), 70.38 (C-3), 74.40 (C-2), 79.29 (C-4), 92.58 (C-1), 169.34, 169.48, and 170.51 (3 C=O).

*2,3-*O*-Isopropylidene-5-*O*-(*p*-nitrobenzoyl)-β-* (**9**) and *-α-*D*-ribofuranosyl azide* (**10**).—2,3-*O*-Isopropylidene-5-*O*-(*p*-nitrobenzoyl)-β-D-ribofuranosyl bromide [8] (**8**; 5.20 g, 12.9 mmol) was added to an ice-cooled suspension of NaN_3 (2.42 g, 37.2 mmol) in hexamethylphosphoric triamide (23 mL). The mixture was stirred for 1 h in an ice bath, then poured into water (200 mL), and extracted with 3:2 ether–EtOAc (200 mL) and ether (2 × 120 mL). The combined extracts were washed with water (150 mL), dried (Na_2SO_4), and concentrated to give a mixture (4.69 g) of **9** and **10**. Fractional crystallisation from *tert*-butyl methyl ether yielded **10** (3.33 g), still slightly contaminated with **9**. The residue, obtained after concentration of the mother liquor, was chromatographed on silica gel (140 g) with 1:4:10 CH_2Cl_2–ether–pentane (1200 mL), followed by ether (300 mL) to give, first, **9** (0.45 g), R_F 0.37 (1:2 ether–hexane), and **10** (0.59 g), R_F 0.13.

Crystallisation of crude **9** from 1:1 *tert*-butyl methyl ether–EtOH gave **9** (0.42 g, 9%) as large light-yellow plates with mp 121–121.5°, $[\alpha]_D^{25}$ −165° (*c* 1.0, $CHCl_3$); ν_{max}^{KBr} 2110 (N_3), 1729, 1528, 1348, 1290, 1235, 1213, 1093, 1084, 1010, 943, 888, and 717 cm^{-1}. NMR data: ^1H, δ 1.34 and 1.52 (2 s, each 3 H, CMe_2), 4.48 (dd, 1 H, H-5a), 4.55 (dd, 1 H, H-5b), 4.57 (d, 1 H, H-2), 4.65 (ddd, 1 H, H-4), 4.80 (dd, 1 H, H-3), 5.62 (s, 1 H, H-1), 8.24–8.34 (AABBm, 4 H, Ar-H), $J_{2,3}$ 5.9, $J_{3,4}$ 1.1, $J_{4,5a}$ 6.8, $J_{4,5b}$ 5.9, $J_{5a,5b}$ 11.6 Hz; ^{13}C, δ 24.94 and 26.39 [$C(CH_3)_2$], 65.08 (C-5), 81.74 (C-3), 84.93 (C-4), 85.33 (C-2), 96.87 (C-1), 113.41 [$C(CH_3)_2$], 123.56, 130.79, 134.82, and 150.63 (Ar–C), 164.18 (C=O).

Anal. Calcd for $C_{15}H_{16}N_4O_7$ (364.32): C, 49.45; H, 4.43; N, 15.38. Found: C, 49.64; H, 4.56; N, 15.49.

Crystallisation of crude **10** from *tert*-butyl methyl ether gave **10** (3.43 g, 73%) as long light-yellow needles with mp 100–101°, $[\alpha]_D^{25}$ +11.5° (*c* 1.0, $CHCl_3$); ν_{max}^{KBr} 2121 (N_3), 1720, 1528, 1349, 1277, 1260, 1212, 1125, 1080, 1009, 884, and 718 cm^{-1}. NMR data: ^1H, δ 1.39 and 1.63 (2 s, each 3 H, CMe_2), 4.48 (dd, 1 H, H-5a), 4.53 (dd, 1 H, H-5b), 4.59 (ddd, 1 H, H-4), 4.77 (dd, 1 H, H-3), 4.83 (dd, 1 H, H-2), 5.13 (d, 1H, H-1), 8.17–8.21 and 8.30–8.34 (AABBm, 4 H, Ar–H), $J_{1,2}$ 4.2, $J_{2,3}$ 6.5, $J_{3,4}$ 2.1, $J_{4,5a}$ 4.4, $J_{4,5b}$ 4.7, $J_{5a,5b}$ 11.9 Hz; ^{13}C, δ 24.85 and 25.61 [$C(CH_3)_2$], 65.07 (C-5), 80.40 (C-4), 81.10 (C-3), 81.16 (C-2), 90.52 (C-1), 115.10 [$C(CH_3)_2$], 123.62, 130.68, 134.61, and 150.63 (Ar–C), 164.12 (C=O).

Anal. Calcd for $C_{15}H_{16}N_4O_7$ (364.32): C, 49.45; H, 4.43; N, 15.38. Found: C, 49.62; H, 4.30; N, 15.50.

2,3-O-Isopropylidene-α-D-ribofuranosyl azide (**7**).—*(a) By deacylation of* **10**. A solution of **10** (3.34 g, 9.17 mmol) in MeOH (330 mL), pre-saturated with NH_3 at 0°, was stirred in an ice bath for 10 h, then concentrated, and the residue was extracted with ether (2 × 100 mL). The combined extracts were concentrated and the residue was chromatographed on silica gel (95 g) with ether to give **7** (1.83 g, 93%), isolated as an almost colorless liquid, R_F 0.42 (ether), $[\alpha]_D^{25}$ +57.5° (*c* 1.0, $CHCl_3$); ν_{max}^{KBr} 2120 (N_3), 1381, 1259, 1213, 1109, 1083, 998, 882, and 857 cm^{-1}. NMR data: ^1H, δ 1.37 and 1.61 (2 s, each 3 H, CMe_2), 2.3 (bs, 1 H, OH), 3.71 (dd, 1 H, H-5a), 3.82 (dd, 1 H, H-5b), 4.31 (m, 1 H, H-4), 4.72–4.78 (m, 2 H, H-2,3), 5.16 (d, 1 H, H-1), $J_{1,2}$ 3.7, $J_{4,5a}$ 3.9, $J_{4,5b}$ 3.2, $J_{5a,5b}$ 11.7 Hz; ^{13}C, δ 24.82 and 25.61 [$C(CH_3)_2$], 63.14 (C-5), 81.02 and 81.40 (C-2,3), 83.25 (C-4), 90.89 (C-1), 114.65 [$C(CH_3)_2$].

Anal. Calcd for $C_8H_{13}N_3O_4$ (215.21): N, 19.53. Found: N, 19.68.

(b) By isopropylidenation [15] *of α-D-ribofuranosyl azide* (**6**). To a solution of **6** (350 mg, 2 mmol) in acetone (20 mL) was added iodine (100 mg), and the solution was stirred at room temperature for 2 h. The catalyst was destroyed by the addition of aq 5% $Na_2S_2O_3$ (5 mL), the acetone was evaporated, and the residue was diluted to ~ 20 mL with water. The solution was extracted with ether (3 × 20 mL), and the combined extracts were dried ($CaSO_4$) and concentrated to provide **7** (395 mg, 92%) as an almost colorless liquid, $[\alpha]_D^{25}$ +57° (*c* 1.0, $CHCl_3$), identical with the compound prepared from **10**.

α-D-*Ribofuranosyl azide* (**6**).—*(a) By deisopropylidenation of* **7**. To a solution of **7** (1.50 g, 7 mmol) in water (3.5 mL) and tetrahydrofuran (5 mL) was added Dowex 50W-X8 (H^+) resin (2 mL), pre-washed with MeOH and water. The mixture was stirred at room temperature for 1 day, then filtered, the resin was washed with MeOH, and the combined filtrate and washings were concentrated. Chromatography of the residue on silica gel (100 g) with 5:1 ether–acetone gave **6** (0.66 g, 54%), isolated as a colorless syrup, R_F 0.33, $[\alpha]_D^{25}$ +212° (*c* 1.0, acetone); ν_{max}^{KBr} 2122 (N_3), 1637, 1408, 1338, 1254, 1129, 1086, 1040, and 624 cm^{-1}. NMR data: ^1H (Me_2SO-d_6, D_2O treated), δ 3.46 (dd, 1 H, H-5a), 3.58 (dd, 1 H, H-5b), 3.93 (dd, 1 H, H-3), 4.00 (ddd, 1 H, H-4), 4.07 (dd, 1 H, H-2), 5.14 (d, 1 H, H-1), $J_{1,2}$ 4.5, $J_{2,3}$ 5.3, $J_{3,4}$ 5.2, $J_{4,5a}$ 4.6, $J_{4,5b}$ 3.2, $J_{5a,5b}$ 12.2 Hz; ^{13}C (Me_2SO-d_6, δ 39.50), δ 61.29 (C-5), 69.79 (C-3), 72.60 (C-2), 85.53 (C-4), 90.64 (C-1).

Anal. Calcd for $C_5H_9N_3O_4$ (175.15): C, 34.29; H, 5.18; N, 23.99. Found: C, 34.47; H, 5.32; N, 23.78.

(b) By deacylation of **5**. Compound **5** was *O*-debenzoylated with methanolic NaOMe, as described [5a] for its *β* anomer. The product (85%) had $[\alpha]_D^{25}$ +208.5° (*c* 1.0, acetone) and was identical with the compound prepared from **7**.

ACKNOWLEDGMENTS

This investigation was supported by the US–Yugoslav Joint Board, NSF Grant JFP 459, and the Ministry of Science and Technology of Slovenia.

REFERENCES

1 H. Paulsen, Z. Györgydeák, and M. Friedmann, *Chem. Ber.*, 107 (1974) 1568–1578.
2 M.W. Logue and B.H. Han, *Carbohydr. Res.*, 121 (1983) 287–297.
3 W. Schörkhuber and E. Zbiral, *Liebigs Ann. Chem.*, (1980) 1455–1469.
4 F.J. Schendel and J. Stubbe, *Biochemistry*, 25 (1986) 2256–2264.
5 (a) J. Baddiley, J.G. Buchanan, R. Hodges, and J.F. Prescott, *J. Chem. Soc.*, (1957) 4769–4774; (b) R. Carrington, G. Shaw, and D.V. Wilson, *ibid.*, (1965) 6864–6870; (c) W.A. Szarek, O. Achmatowicz, Jr., J. Plenkiewicz, and B.K. Radatus, *Tetrahedron*, 34 (1978) 1427–1433.
6 M.J. Camarasa, R. Alonso, and F.G. de las Heras, *Carbohydr. Res.*, 83 (1980) 152–156.
7 L.B. Townsend, in W.W. Zorbach and R.S. Tipson (Eds.), *Synthetic Procedures in Nucleic Acid Chemistry*, Vol. 2, Wiley–Interscience, New York, 1973, pp 323–340.
8 S. DeBernardo and M. Weigele, *J. Org. Chem.*, 41 (1976) 287–290.
9 Z. Györgydeák, I. Ling, and R. Bognár, *Liebigs Ann. Chem.*, (1983) 279–289.
10 Z. Györgydeák and L. Szilágyi, *Liebigs Ann. Chem.*, (1986) 1393–1397.
11 L.J. Wilson and D. Liotta, *Tetrahedron Lett.*, 31 (1990) 1815–1818.
12 S. Murata, M. Suzuki, and R. Noyori, *Tetrahedron*, 44 (1988) 4259–4275.
13 E.F. Recondo and H. Rinderknecht, *Helv. Chim. Acta*, 42 (1959) 1171–1173.
14 R.D. Guthrie and S.C. Smith, *Chem. Ind. (London)*, (1968) 547–548.
15 K.P.R. Kartha, *Tetrahedron Lett.*, 27 (1986) 3415–3416.