2.0 (br s, 1 H, bridgehead), 2.1 (s, 2 H, $NH_2$), 2.2 (s, 1 H, bridgehead), 2.8 (m, 1 H, $CHNH_2$).

**3-(*p*-Tolylthio)-2-methyl-1-aminopropane.** 3-(*p*-Tolylthio)-2-methyl-1-propene (12 mmol, 2.14 g) was hydroborated with $BH_3$–THF (4 mmol) for 1 h. The amination was carried out as described in the general procedure to yield 0.67 g (85%) of 3-(*p*-tolylthio)-2-methyl-1-aminopropane; mass spectrum, *m/e* 195.3 (calcd 195.3); NMR ($CDCl_3$) $\delta$ 1.1 (t, 3 H, $CH_3$), 1.4–1.8 (m, 3 H, CH and $NH_2$), 2.2 (s, 3 H, $ArCH_3$), 2.5–3.0 (br m, 4 H, $CH_2S$ and $CH_2NH_2$), 7.1 ($A_2X'X_2'$, 4 H, ArH).

**3-[3,4-(Methylenedioxy)phenyl)]-1-aminopropane.** Safrole (30 mmol, 4.87 g) was hydroborated with $BH_3$–THF (10 mmol) for 1 h. The amination was carried out as described in the general procedure to yield 1.71 g (96%) of 3-[3,4-(methylenedioxy)-phenyl]-1-aminopropane;[12] melting point of picrate derivative, 150 °C; mass spectrum, *m/e* 179.7 (calcd 179.2); NMR ($CDCl_3$) $\delta$ 1.5–2.2 (m, 6 H, Ar $CH_2CH_2CH_2NH_2$ and $NH_2$), 2.5–2.7 (m, 2 H, $CH_2NH_2$), 5.9 (s, 2 H, $OCH_2O$), 6.7 (s, 3 H, ArH).

**Methyl 11-Aminoundecanoate.** Methyl 10-undecenoate (30 mmol, 5.95 g) was hydroborated with $BH_3$–THF (10 mmol) for 1 h. The amination was carried out as described in the general procedure to yield 1.64 g (76%) of methyl 11-aminoundecanoate; melting point of picrate derivative, 112 °C; mass spectrum, *m/e* 215 (calcd 215.3); NMR ($CDCl_3$) $\delta$ 1.1–1.6 (s, 16, alkyl), 1.8–2.4 (m, 4 H, $CH_2C{=}O$ and $NH_2$), 2.6–2.9 (m, 2 H, $CH_2NH_2$), 3.7 (s, 3 H, $OCH_3$).

**Acknowledgment.** We thank the Department of Energy (DE-AS05-80-EV10363) for support of this research.

**Registry No.** 1-Octene, 111-66-0; 1-decene, 872-05-9; cyclohexene, 110-83-8; 2-methyl-1-pentene, 763-29-1; norbornene, 498-66-8; 3-(*p*-tolylthio)-2-methyl-1-propene, 54844-24-5; safrole, 94-59-7; methyl 10-undecanoate, 111-81-9; triacetylborane, 3248-78-0; tridecylborane, 1188-96-1; tricyclohexylborane, 1088-01-3; tri(2-methylpentan-1-yl)-borane, 1188-50-7; tri-2-norbornylborane, 14289-75-9; tri[3-(*p*-tolylthio)-2-methylpropan-1-yl]borane, 78498-53-0; tri[3-(1,3-benzodioxol-5-yl)propan-1-yl]borane, 78498-54-1; tri[(10-carboxymethoxy)-decan-1-yl]borane, 63399-92-8; 1-aminooctane, 111-86-4; 1-aminooctane picrate, 78498-55-2; 1-aminodecane, 2016-57-1; 1-aminodecane picrate, 78498-56-3; aminocyclohexane, 108-91-8; aminocyclohexane picrate, 17623-38-0; 1-amino-2-methylpentane, 13364-16-4; 1-amino-2-methylpentane picrate, 78498-57-4; 2-aminonorbornane, 822-98-0; 2-aminonorbornane picrate, 1485-53-6; 3-(*p*-tolylthio)-2-methyl-1-aminopropane, 78498-58-5; 3-[3,4-(methylenedioxy)phenyl]-1-aminopropane, 78498-59-6; 3-[3,4-(methylenedioxy)phenyl]-1-aminopropane picrate, 78498-60-9; 1-[3,4-(methylenedioxy)-phenyl]-2-aminopropane, 4764-17-4; methyl 11-aminoundecanoate, 28691-27-2; methyl 11-aminoundecanoate picrate, 78498-61-0; ammonium hydroxide, 1336-21-6.

(12) The product contains approximately 15% of the 2-amino derivative. This is a result of the decrease in regioselectivity of the hydroboration reaction due to the inductive effect of the phenyl ring. Primary amines synthesized via this method normally contain only small amounts of the 2-amino isomer.

## Aminoglycoside Antibiotics. 4. Regiospecific Partial Synthesis of Ribostamycin and 4″-Thioribostamycin

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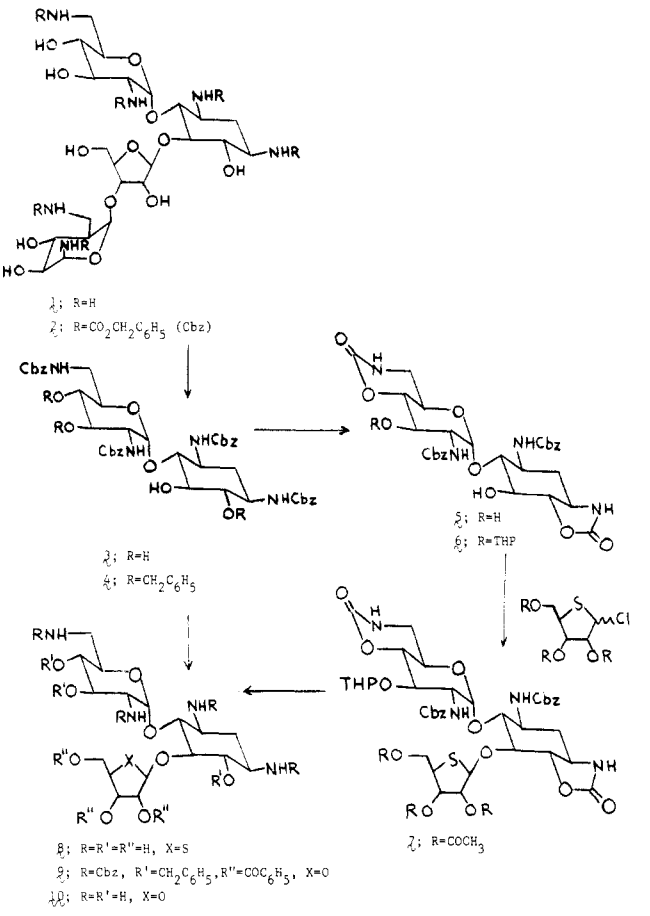
In an earlier paper in this series we described the regiospecific synthesis of ribostamycin (**10**) from neamine.[1] This synthesis was based on protecting the functional groups of neamine in such a manner that only the 5-hydroxyl group was free for glycosidic linking with a suitable 1-ribosyl chloride. In order to obtain the appropriately protected neamine derivative (**6**), we treated tetra-*N*-(carbobenzyloxy)neamine (**3**) with sodium hydride to give a bis(cyclic carbamate) derivative **5**, which had both the 6- and 3′-hydroxyl groups free (see Scheme I). Selective protection of the 3′-hydroxyl group was surprisingly effective with dihydropyran and *p*-toluenesulfonic acid. The product **6** was obtained in 80% yield. In fact, all of the steps in the synthesis of ribostamycin went in satisfactory yield except for the final deprotection, which gave 19% for the sequence of alkaline hydrolysis and catalytic hydrogenolysis.[1]

Scheme I



With a good synthesis of **6** accomplished, it was desirable to establish its further utility for aminoglycoside synthesis. One structure that interested us was the 4″-thio analogue **8** of ribostamycin. No thioaminoglycosides had been prepared prior to the start of our investigation (although one investigation[2] has been published in the meantime). We anticipated that the 4″-thio analogue would be biologically active by analogy to the good antibacterial activity observed when 4-thioribose was used in place of ribose in certain purine nucleosides.[3,4] Thus, 2,3,5-tri-*O*-acetyl-4-thioribosyl 1-chloride was prepared by the published method[5] and treated with **6**, mercuric cyanide, and Drierite in methylene chloride. The reaction went to completion and workup gave 58% of protected 4″-thioribostamycin derivative **7**, obtained as a single anomer. This anomer is presumed to be $\beta$ according to the trans rule.[3] Deprotection by barium hydroxide hydrolysis and catalytic hy-

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drogenolysis gave the desired 4″-thioribostamycin (8), but again the yield was low (12%). Compound 8 was screened against a variety of species of bacteria, but it was surprisingly inactive against all of them, in contrast to ribostamycin (10). This observation casts some doubt on β stereochemistry for the glycoside linkage. However, the relatively close optical rotations of 8 and authentic ribostamycin (10) supported the stereochemical assignment. The specific rotation of 8 was $[\alpha]^{26}_{546}$ +47.8° (c 1.0, $H_2O$) and that of 10 was $[\alpha]^{26}_{546}$ +37.8° (c 1.0, $H_2O$).

Concern for the low yields obtained in the deprotection of the precursors for both 8 and 10 led us to examine alternative blocking groups. In particular, it seemed desirable to avoid the hydrolysis step in strong barium hydroxide solution. We also were interested in exploring the possibility of protecting neomycin before it was hydrolyzed to neamine. If this could be done, it would provide an unambiguous synthesis of neamine protected on every functional group except the 5-hydroxyl, which is liberated in the hydrolysis. The synthesis of ribostamycin was chosen to explore the potential of this approach. Thus, neomycin (1) was converted into its hexa-*N*-carbobenzyloxy derivative 2 in 91% yield.[6] Treatment of 2 with benzyl bromide and barium hydroxide in DMF, followed by hydrolysis with methanolic hydrogen chloride, gave the desired tri-*O*-benzyl-tetra-*N*-(carbobenzyloxy) derivative (4) of neamine in 50% yield. This simple and unambiguous synthesis provided an intermediate with good solubility in chloroform which was suitable for Koenings–Knorr coupling with 2,3,5-tri-*O*-benzoylribosyl 1-chloride. The product of this reaction, ribostamycin derivative 9, was obtained pure in 35% yield. Removal of the benzoyl groups with sodium methoxide, followed by catalytic hydrogenolysis of the benzyl and carbobenzyloxy groups, gave ribostamycin which was identical in infrared spectrum and $R_f$ values in two solvent systems with an authentic sample. Unfortunately, the 21% yield obtained in this deprotection process was not significantly better than that of the earlier method. The main advantage of the newer method would appear to be a shorter sequence from the ultimate starting material, neomycin.

## Experimental Section

Melting points were determined on a Mel-Temp apparatus and are uncorrected. Infrared spectra were determined on a Beckman IR-33 spectrophotometer as KBr pellets. Nuclear magnetic resonance spectra were recorded on a Varian EM-360 spectrometer using $Me_4Si$ as the standard. Optical rotations were taken on a Carl Zeiss OLD4 automatic polarimeter under the indicated conditions. Elemental analyses were performed by Chemalytics, Inc.

**3,2′-Di-*N*-(benzyloxycarbonyl)-3′-*O*-(tetrahydropyranyl)-2″,3″,5″-tri-*O*-acetyl-1,6:6′,4′-*N*,*O*-carbonylthioribostamycin (7).** A solution of 6 (0.73 g, 1 mmol) in 10 mL of dry methylene chloride was treated with dry mercuric cyanide (0.70 g, 2.8 mmol) and predried powdered Drierite (5.0 g). The mixture was stirred 16h under $N_2$ and then treated with a solution of 2,3,5-tri-*O*-acetyl-D-4-thioribofuranosyl chloride[5] (0.80 g, 2.6 mmol) in 3 mL of methylene chloride. The mixture was stirred at reflux temperature for 4 days and filtered through a pad of Celite. This pad was washed thoroughly with methylene chloride, and the combined filtrate and washes were concentrated to a small volume and treated with ether. The solid that formed was purified by chromatography on silica gel with benzene–ethyl acetate as the solvent. Recrystallization of the product from chloroform–petroleum ether gave 0.58g (58%) of 7 as nearly white solid: mp 149–152 °C dec; $[\alpha]^{26}_{546}$ +29.9° (c 1.0, $CHCl_3$); IR 1765 (five-membered carbamate), 1730, 1720, 1715 (OAc and six-membered carbamate), 1710 (NHCO I), 1695 $cm^{-1}$ (NHCO II); NMR ($CDCl_3$) δ 1.2–1.8 (6, THP), 2.0 (9, OAc), 5.10 (6, benzylic), 5.4 and 5.8 (anomeric), 7.30 (br, aromatic).

Anal. Calcd for $C_{46}H_{56}N_4O_{19}S$: C, 68.91; H, 5.86; N, 4.87. Found: C, 69.19; H, 5.87; N, 5.01.

**4″-Thioribostamycin (8).** A solution of 7 (0.48 g, 0.48 mmol) in 10 mL of dioxane was treated with 10 mL of 1 M aqueous barium hydroxide, and the mixture was stirred at 60 °C for 2 h. Two more 10-mL portions of barium hydroxide solution were added at 2-h intervals. The mixture was cooled, neutralized with $CO_2$ and filtered. The residue was washed thoroughly with DMF, and these washes were combined and concentrated under reduced pressure. No acetate or cyclic carbamate absorption peaks were seen in the IR spectrum.

The crude product was dissolved in 20 mL of 50% aqueous dioxane, treated with 10% palladium-on-charcoal (150 mg) and 2 mL of acetic acid, and shaken with hydrogen for 16 h. The mixture was filtered and concentrated. Examination of the residue by TLC (1:4:2:1 chloroform–methanol–27% ammonium hydroxide–water on silica gel) showed incomplete hydrogenolysis. The catalytic hydrogenation was repeated with only water as the solvent. After a workup by filtration and concentration, the crude product was kept over Amberlite IR-400 ($OH^-$) at 0 °C for 1 h. Chromatography in the system described above showed only one main spot. The product was purified on Amberlite CG-50 ($NH_4^+$) with 0–1 M ammonium hydroxide. Concentration of the main fraction gave a solid that was crystallized from methanol–acetone. This procedure gave 26 mg (11.5%) of 8 as the dicarbonic acid dihydrate, a nearly white solid: mp 225 °C dec; $[\alpha]^{26}_{546}$ +48.7° (c 1.0, $H_2O$); IR (KBr) 3600–3000 $cm^{-1}$ (OH and NH); NMR ($D_2O$) δ 5.5 (br s, anomeric proton), 6.30 (br d, $J$ = 3 Hz, anomeric proton in thioribosyl ring).

Anal. Calcd for $C_{17}H_{34}N_4O_9S\cdot 2H_2CO_3\cdot 2H_2O$: C, 35.96; H, 6.66; N, 8.82; S, 5.05. Found: C, 36.00; H, 6.35; N, 8.48; S, 4.72.

**Hexa-*N*-(benzyloxycarbonyl)neomycin B (2).**[6] A solution of neomycin sulfate (1.0 g, 1.3 mmol) in 30 mL of 75% aqueous methanol was treated with sodium carbonate (2.0 g, 18.9 mmol). The mixture was cooled to 0 °C and treated with a solution of carbobenzyloxy chloride (2.25 g, 13.2 mmol) in a small amount of methanol. This mixture was stirred 3 h at 0 °C and concentrated under reduced pressure. The solid residue was extracted three times with hot acetone, and the combined extracts were concentrated to dryness. Crystallization of the residue from ethyl acetate–petroleum ether gave 1.7 g (91%) of 2 as white solid: mp 118–120 °C dec; $[\alpha]^{26}_{546}$ +34.1° (c 1.0, $CHCl_3$); IR 1720, 1710, 1700, 1694 (NHCO I), 1530 $cm^{-1}$ (NHCO II); NMR ($CDCl_3$) δ 5.10 (benzylic), 7.30 (aromatic).

Anal. Calcd for $C_{71}H_{82}N_6O_{25}$: C, 60.08; H, 5.78; N, 5.92. Found: C, 59.71; H, 6.01; N, 5.86.

**1,3,2′,6′-Tetra-*N*-(benzyloxycarbonyl)-6,3′,4′-tri-*O*-benzylneamine (4).** A solution of 2 (2.0 g, 1.4 mmol) in 30 mL of DMF was treated with barium oxide (10.1 g) and barium hydroxide octahydrate (13.0 g). The mixture was cooled at 0 °C and treated dropwise with excess benzyl bromide (8.0 mL). The resulting mixture was stirred 2 h at 0 °C and then 18 h at 25 °C. It was diluted with chloroform, filtered, and concentrated under reduced pressure. The resulting yellow oil was triturated with petroleum either to remove unreacted benzyl bromide. This procedure gae the perbenzyl derivative as a semisolid that was used directly in the next step.

The perbenzyl derivative was dissolved in 50 mL of methanol, and dry hydrogen chloride was passed into this solution for 15 min. The mixture was heated at reflux 48 h, cooled, and concentrated. A chlorofrom solution of the residue was washed with water and with dilute sodium bicarbonate, dried over sodium sulfate, and concentrated. The resulting solid was purified two times by chromatography on a silica gel column with benzene–ethyl acetate as solvent. Recrystallization from chloroform–petroleum ether gave 0.80 g (50%) of 4 as the monohydrate: mp 130–132 °C dec; $[\alpha]^{26}_{546}$ +41.2° (c 1.0, $CHCl_3$); IR (KBr) 1710, 1700, 1690 (NHCO I), 1525 $cm^{-1}$ (NHCO II); NMR ($CDCl_3$) δ 4.70 (6, benzyl), 7.20 (aromatic).

Anal. Calcd for $C_{65}H_{68}N_4O_{14}\cdot H_2O$: C, 68.05; H, 6.15; N, 4.88. Found: C, 67.87; H, 6.10; N, 4.90.

(6) Preparation of the *N*-carbobenzyloxy derivative of neomycin B has been reported previously, but experimental details were not given (Umezawa, S. *Adv. Carbohydr. Chem. Biochem.* **1974**, *31*, 111. Hanessian, S.; Masse, R.; Capmeau, M. L. *J. Antibiot.* **1977**, *30*, 894).

**1,3,2′,6′-Tetra-*N*-(benzyloxycarbonyl)-2″,3″,5″-tri-*O*-benzoyl-6,3′,4′-tri-*O*-benzylribostamycin (9).** A mixture of **4** (0.23 g, 0.2 mmol), mercuric cyanide (0.16 g, 0.62 mmol), Drierite (2.0 g), and anhydrous chloroform (5 mL) was stirred 16 h at 25 °C. A solution of 2,3,5-tri-*O*-benzoyl-D-ribofuranosyl chloride[7] (0.19 g, 0.39 mmol) in 3 mL of chloroform was added, and the mixture was stirred 72 h at reflux. It was filtered through Celite and concentrated to dryness. The solid residue was purified by chromatography on a silica gel column with benzene–ethyl acetate as solvent and then recrystallized from chloroform–hexane to give 0.11 g (35%) of **9** as white solid: mp 132–135 °C; $[\alpha]^{26}_{546}$ +43.4° (*c* 1.0, $CHCl_3$); IR (KBr) 1720 (benzoate), 1710, 1700, 1695 (NHCO I), 1520 $cm^{-1}$ (NHCO II); NMR ($CDCl_3$) $\delta$ 4.17 (benzyl), 5.40 and 5.60 (anomeric protons), 6.9–8.15 (aromatic).

Anal. Calcd for $C_{91}H_{88}N_4O_{21}$: C, 69.45; H, 5.63; N, 3.56. Found: C, 69.37; H, 5.53; N, 3.88.

**Ribostamycin (10).** A solution of sodium methoxide, prepared from 10 mg of sodium and 10 mL of dry methanol, was treated with **9** (25 mg). After 3.5 h the mixture was neutralized with acetic acid and concentrated under reduced pressure. The residual solid was dissolved in 20 mL of 50% aqueous dioxane, treated with 10% palladium-on-carbon (50 mg) and 2 mL of acetic acid, and shaken with hydrogen for 48 h. The mixture was filtered through Celite and concentrated. TLC of the residue showed that hydrogenolysis was incomplete. The hydrogenation was repeated as described above, except that the solvent was only water. A workup in the same manner gave a solid that was purified by chromatography on Amberlite IR-C-50 ($NH_4^+$) with 0–0.5 M ammonium hydroxide as the solvent, followed by chromatography on Amberlite IR-400 ($OH^-$) with water as the solvent. These procedures gave 1.52 mg (21%) of **10** as a white solid that was identical with an authentic sample from Mieji Laboratories in IR absorption spectrum and TLC in the systems chloroform–methanol–28% ammonium hydroxide–water (1:4:2:1) and the upper phase of chloroform–methanol–28% ammonium hydroxide (1:1:1).

**Acknowledgment.** This investigation was begun at Purdue University and supported in part by a grant from the Purdue Research Foundation. We thank Bristol Laboratories for a sample of ribostamycin and for assaying the antibacterial activity of 4″-thioribostamycin.

**Registry No.** 1·$H_2SO_4$, 28002-70-2; **2**, 58096-78-9; **4**, 78763-85-6; **6**, 66787-83-5; **7**, 78763-86-7; 8·$2H_2CO_3$, 78763-88-9; **9**, 78763-89-0; **10**, 25546-65-0; 2,3,5-tri-*O*-acetyl-D-4-thioribofuranosyl chloride, 59042-15-8; carbobenzyloxy chloride, 501-53-1; 2,3,5-tri-*O*-benzoyl-D-ribofuranosyl chloride, 5991-01-5.

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## Synthesis of 2′-Deoxynucleosides by Deoxygenation of Ribonucleosides

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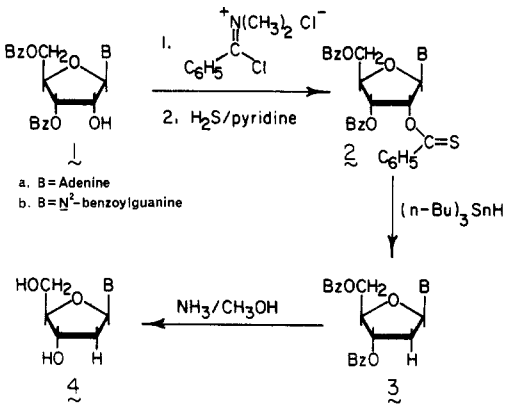
A recent communication by Robins and Wilson[2] prompts us to report an alternative method for the conversion of ribonucleosides to 2′-deoxyribonucleosides that may offer certain advantages when applied to the synthesis of analogues of naturally occurring 2′-deoxyribonucleosides.

One of the major drawbacks in the direct synthesis of 2-deoxyribofuranosyl derivatives of synthetic analogues of the naturally occurring purine bases is the formation of a mixture of anomers upon condensation of the heterocyclic base with an appropriately protected derivative of 2-deoxyribofuranose.[3] On the other hand, synthesis of the corresponding ribofuranosyl derivatives proceeds with high stereoselectivity to give almost exclusively the desired $\beta$ anomer, an effect which is generally attributed to the intramolecular participation of the acyl protecting group employed on the 2-hydroxyl group of the sugar.[4] It was our purpose to utilize the stereoselectivity in the condensation step to provide the desired $\beta$ anomer and then to deoxygenate selectively at the 2′-position.

Scheme I




Selective deoxygenation of nucleosides has been difficult to realize in the past. Most approaches have relied upon intramolecular displacement of a derivatized 2′-hydroxyl group followed by reductive ring opening[5] or upon ring opening of a bridged intermediate by halide ion followed by reductive dehalogenation.[6] In order to develop a general, efficient procedure for 2′-deoxygenation under reasonably mild conditions, we selected homolytic cleavage of the 2′-carbon–oxygen bond via tri-*n*-butyltin hydride reduction of a thioester derivative as demonstrated by Barton et al.[7] Ribonucleosides suitably protected by acyl groups on the 3′- and 5′-hydroxyls were prepared by regioselective deacylation of fully acylated nucleosides with hydroxylaminium acetate in dry pyridine according to the method of Ishido et al.[8] This approach seems particularly appropriate for the synthesis of unnatural nucleoside analogues, since fully acylated nucleosides generally result from most ribosidation procedures applied to heterocyclic bases and since direct removal of only the 2′-*O*-acyl group avoids the necessity for total deprotection followed by introduction of a new protection scheme. Additionally, the demonstrated applicability of the selective deprotection method to both purine and pyrimidine ribonucleosides makes it an effective, general step in the synthesis of 3′,5′-diprotected ribonucleosides suitable for use in subsequent deoxygenation procedures. Whether the observed selectivity in the 2′,3′,5′-tri-*O*-acyl cleavage to the 3′,5′-di-*O*-acyl ribonucleoside is due to the conversion of the

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