Table III
Effect of Solvent on the Mole Fraction of *cis*-Succinimide Units in NPM-CEVE Copolymers[a]

solvent	mole fraction *cis*-succinimide units (χ_c)
none	0.852[b]
benzene	0.505[b]
CH_2Cl_2	0.633

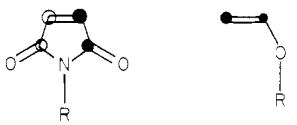
[a] Polymerization conditions: χ_M = 0.5, AIBN, 60 °C. [b] Peak areas estimated by peak intensities.

the comonomers, as measured by the parameter K_s.

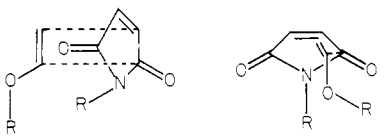
The equilibrium constant for complex formation is generally solvent dependent.[3] Copolymers prepared in different solvents exhibited widely varying stereochemistry. This effect is shown in Table III, which includes the χ_c values for NPM–CEVE copolymers prepared under similar conditions except for solvent. Since benzene is known to form complexes with NPM,[8] the results may be explained as being due to competition between solvent and CEVE monomer for acceptor NPM. The overall concentration of NPM–CEVE complexes would thus be reduced, causing a decrease in copolymer stereoregularity.

Copolymers of N-substituted maleimides and vinyl ethers have stereochemistry that is predominantly cis (erythro) at the succinimide units, while the relative stereochemistry between the other chiral centers in the copolymer backbone (vinyl ether–maleimide junction bonds) is essentially random. The stereoselectivity varies with such copolymerization conditions as temperature, solvent, total monomer concentration, comonomer concentration ratio at fixed total monomer concentration, and the donor–acceptor character of the comonomer pair in the same way as might be expected if it were related to the ease of formation of charge-transfer complexes between the comonomers.

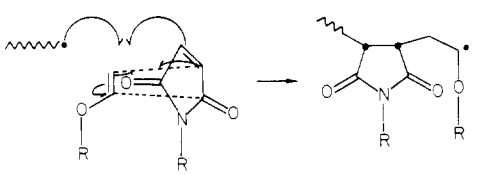
Mulliken theory[3] predicts that the most probable geometry of a charge-transfer complex is that in which there is maximum overlap between the HOMO of the donor and the LUMO of the acceptor. The LUMO of maleimide monomers[9] and the HOMO of vinyl ethers are depicted below.



Thus, the expected geometry of the complex may be visualized as



The stereochemical results discussed above may be rationalized by invoking attack of the radical chain end on the side of the complex that is syn to the vinyl ether.



This mechanism is, in effect, a concerted addition of the complex to the chain end. The next complex could conceivably add to either side of the vinyl ether radical, thus explaining the random relative stereochemistry between the vinyl ether methine carbon and the methines of adjacent succinimide units observed in the copolymers.

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Registry No. CEVE, 110-75-8; NPM, 941-69-5; *N*-(*p*-C_6H_4CN)maleimide, 31489-18-6; *N*-(*p*-$C_6H_4CF_3$)maleimide, 54647-09-5; *N*-(*p*-$C_6H_4CO_2Et$)maleimide, 14794-06-0; *N*-(*p*-C_6H_4F)maleimide, 6633-22-3; *N*-(*p*-C_6H_4Cl)maleimide, 1631-29-4; *N*-(*p*-C_6H_4Br)maleimide, 13380-67-1; *N*-(*p*-C_6H_4OAc)maleimide, 6637-46-3; *N*-(*p*-$C_6H_4CH_3$)maleimide, 1631-28-3; *N*-(*p*-$C_6H_4OCH_3$)maleimide, 1081-17-0; *N*-(C_6H_{11})maleimide, 1631-25-0.

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Kurt G. Olson
PPG Industries, Coatings and Resins Division
Allison Park, Pennsylvania 15101

George B. Butler*
Center for Macromolecular Science
and Department of Chemistry
University of Florida, Gainesville, Florida 32611

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Regioselectively Modified Stereoregular Polysaccharides. 6. Synthesis of 3-Deoxy-(1→6)-α-D-*ribo*-hexopyranan[1]

We report a convenient, high-yield procedure for the synthesis of the perfectly 3-deoxygenated linear stereoregular (1→6)-α-D-glucopyranan. According to Scheme I, the free hydroxyl group of 1,6-anhydro-2,4-di-*O*-benzyl-β-D-glucopyranose (**1**) was thioacylated and then reduced with tributylstannane to give 1,6-anhydro-2,4-di-*O*-benzyl-3-deoxy-β-D-*ribo*-hexopyranose (**3**). Ring-opening polymerization of the deoxygenated monomer **3** in the presence of phosphorus pentafluoride (PF_5) at −60 °C followed by debenzylation yielded 3-deoxy-(1→6)-α-D-*ribo*-hexopyranan (**5**).

Deoxy sugars are biologically important, and several reports[2-4] on chemical syntheses of deoxy polysaccharides via polymerization of 1,6-anhydro deoxy sugar derivatives have recently appeared in succession. Most synthetic procedures of these deoxy monomers, however, are tedious and involve long sequences of reactions. In this paper, we employed the mild deoxygenation method developed by Barton et al.[5-7] and obtained the deoxy compound **3** simply and quickly.

Treatment of **1** with *N*,*N*′-(thiocarbonyl)diimidazole in 1,2-dichloroethane gave 1,6-anhydro-2,4-di-*O*-benzyl-3-

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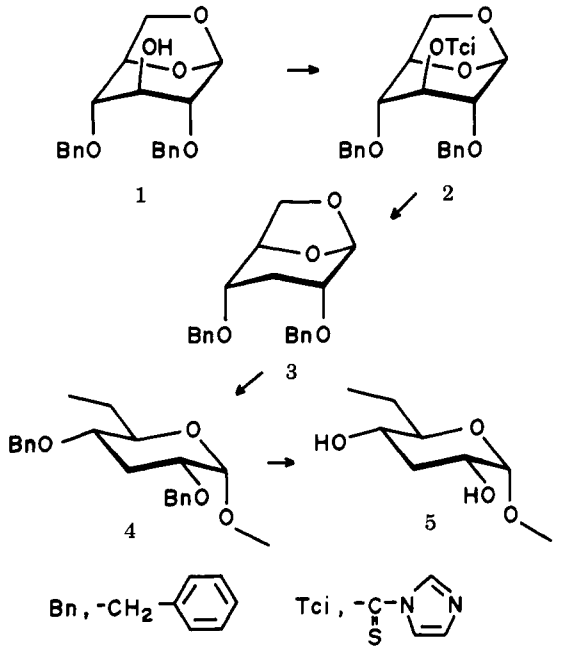
Scheme I
Synthesis of 3-Deoxy-(1→6)-α-D-*ribo*-hexopyranan (5)



O-(thiocarbonyl)imidazolyl-β-D-glucopyranose (**2**) as a syrup in 88% isolated yield: $[\alpha]^{25}_D$ −60.5° (*c* 1 (chloroform)). The ^{1}H NMR spectrum of **2** showed characteristic peaks for the three imidazolyl protons (8.21, 7.52, and 6.98 ppm) and for the H-3 proton attached to the carbon bearing the thiono ester substituent (5.76 ppm). The ^{13}C NMR spectrum also showed signals for the imidazolyl carbons (137.03, 131.22, and 118.18 ppm) and for the thiocarbonyl carbon (182.53 ppm).

Radical-induced reduction of **2** with tributylstannane in refluxing toluene produced a crystalline mixture of **3** and a minor amount of **1**. Sugar **3** was isolated by silica gel chromatography in 79% yield: mp 60–60.5 °C; $[\alpha]^{25}_D$ −49.1° (*c* 1 (chloroform)). The ^{1}H and ^{13}C NMR spectra of **3** confirmed the deoxygenation in position 3. Two H-3 proton signals (H-3_{eq}, 2.0 ppm; H-3_{ax}, 1.8 ppm) and a C-3 carbon signal (24.80 ppm) were found at characteristically higher fields. The β-anomeric H-1 proton at 5.43 ppm as a singlet and the β-C-1 carbon at 100.97 ppm were also distinguishable.

The polymerization of **3** was carried out under high vacuum at −60 °C in anhydrous dichloromethane in the presence of 5.8 mol % of PF_5. After 3 h, the homopolymer with an intrinsic viscosity of 0.56 (in chloroform at 25 °C; *c*, g/100 mL) was obtained in 87.8% yield. In the ^{13}C NMR spectrum, only the α-C-1 signal at 96.39 ppm was observed in the anomeric carbon region and no resonances due to the β-anomeric configuration were detected. The polymerization caused about 5.8 ppm downfield shift of the C-3 methylene resonance, which then appeared at 30.60 ppm. The two methylene groups on the benzyl substituents appeared as one peak at 70.71 ppm. In the ^{1}H NMR spectrum, the α-anomeric proton signal at 4.96 ppm was split into a doublet. These data, together with the high positive optical rotation ($[\alpha]^{25}_D$ +143.5°, in chloroform), indicated that the polymerization occurred stereospecifically to give 2,4-di-*O*-benzyl-3-deoxy-(1→6)-α-D-*ribo*-hexopyranan (**4**).

Conversion of **4** to **5** was accomplished in quantitative yield by the conventional debenzylaton method using sodium in liquid ammonia. Polymer **5** showed a high positive optical rotation ($[\alpha]^{25}_D$ +169°, in water) and moderate intrinsic viscosity ($[\eta]$ = 0.28 dL/g, in water at 25 °C). It

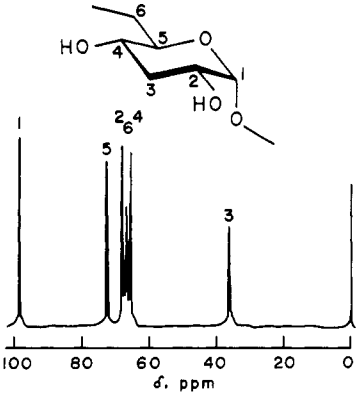


Figure 1. Proton noise decoupled ^{13}C NMR spectrum (25 MHz) of 3-deoxy-(1→6)-α-D-*ribo*-hexopyranan (**5**). Solvent, D_2O; concentration, 12%; 10-mm inside diameter tube; room temperature; 4500 scans; Me_4Si external standard.

was soluble in water, dimethyl sulfoxide, dimethylformamide, and pyridine. The ^{1}H NMR spectrum showed isolated peaks for the two H-3 protons (H-3_{eq}, 2.6 ppm; H-3_{ax}, 2.3 ppm) and the α-anomeric H-1 proton (5.35 ppm, doublet). The ^{13}C NMR spectrum (Figure 1) consists of six peaks that correspond to those of 3-deoxy-(1→6)-α-D-*ribo*-hexopyranan (**5**). The C-3 methylene carbon at 36.11 ppm and the α-anomeric C-1 carbon at 97.80 ppm were distinct. Assignment of the other resonances (72.22, C-5; 67.74, C-2; 66.52, C-6; 65.25, C-4) could be made based on deoxy substituent parameters which were derived for the corresponding monosaccharides, 3-deoxy-α-D-*ribo*-hexopyranose and α-D-glucopyranose.[8] The assignment supports the ^{13}C NMR assignment previously made for partially 3-deoxygenated (1→6)-α-D-glucopyranans,[9] which were prepared by reduction of 3-*O*-acetyl-2,4-di-*O*-benzyl-(1→6)-α-D-glucopyranan with use of sodium in hexamethylphosphoramide.

The present sequence of reactions thus provided smooth and efficient access to the unusual deoxy polysaccharide **5**, which may be of biochemical and biomedical significance.[10] Evaluation of the monomer reactivity of **3** and demonstration of the applicability of **5** are in progress.

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Kazukiyo Kobayashi* and Hiroshi Sumitomo

Faculty of Agriculture, Nagoya University
Chikusa, Nagoya 464, Japan

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