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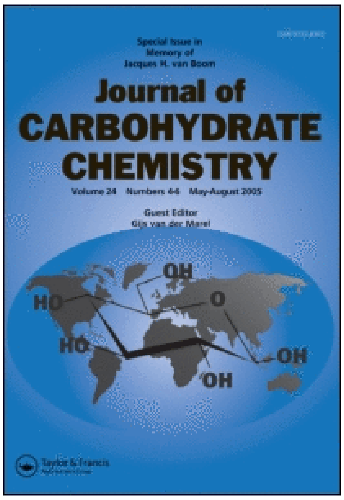

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Use of the Anomeric Carbon-13 Proton One Bond Scalar Coupling Constant as a Tool for Detecting 1,2-Orthoester Formation in Oligosaccharide Synthesis

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COMMUNICATION

USE OF THE ANOMERIC CARBON-13 PROTON ONE BOND SCALAR COUPLING CONSTANT AS A TOOL FOR DETECTING 1,2-ORTHOESTER FORMATION IN OLIGOSACCHARIDE SYNTHESIS

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RESULTS AND DISCUSSION

The anomeric $^{1}J_{C,H}$ value has for some time been successfully used for structural elucidation of oligosaccharides. The first recorded spectra on unenriched carbohydrates were published by Bock *et al.* in 1973 and pointed out that the anomeric $^{1}J_{C,H}$ value could be used for assignment of the anomeric configuration since pyranoses with an axial H-1 have a $^{1}J_{C\text{-}1,H\text{-}1}$ value which is approximately 10 Hz lower than the corresponding value in compounds with an equatorial H-1.[1-3] Their method recording non decoupled ^{13}C NMR spectra had the disadvantage of being insensitive and thereby time-consuming. Introduction of INEPT[4] followed by technical developments, has overcome this disadvantage. Nowadays, with reverse detection techniques, technical skill instead of sensitivity is a limiting factor. In this communication I would like to emphasize that the anomeric $^{1}J_{C,H}$ value can be used for detecting 1,2-orthoester formation as well as for establishing α- or β-configuration.

The various 1,2-orthoesters were made from readily available and crystalline glycosyl donors and acceptors: ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-gluco-

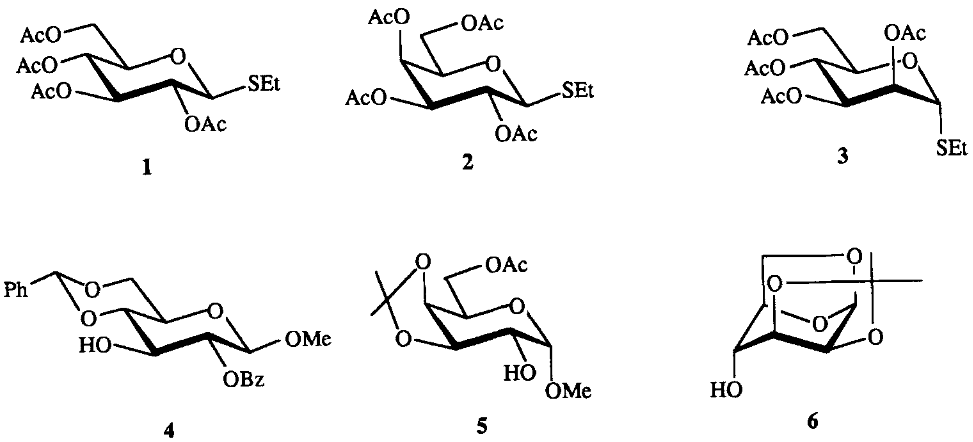

Figure 1

Table 1

Entry	Donor	Acceptor	Yield (%)	$^{1}J_{C\text{-}1',H\text{-}1'}$ (Hz)
1	1	4	91	184
2	1	5	92	185
3	1	6	75	182
4	2	4	60	181
5	2	5	80	181
6	2	6	75	180
7	3	4	65	178
8	3	5	76	177
9	3	6	78	176

pyranoside[5] **1**, ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside[6] **2**, and ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranoside[6] **3** were used as glycosyl donors. Glycosyl acceptors were methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-glucopyranoside[7] **4**, methyl 6-*O*-acetyl-3,4-*O*-isopropylidene-α-D-galactopyranoside[8] **5**, and 1,6-anhydro-2,3-*O*-isopropylidene-β-D-mannopyranose[9] **6**. These are shown in Figure 1.

Table 1 shows that 1,2-orthoesters in the D-*gluco-* and D-*galacto*-series (entry 1-6) have a $^1J_{C\text{-}1',H\text{-}1'}$ value (> 180 Hz) well above the one expected from a β-glycoside (~155-165 Hz) or an α-glycoside (~165-175 Hz). However, in the D-*manno*-series (entry 7-9) the results are more ambiguous. The value (176-178 Hz) is in the range of that for the expected α-glycoside. This difference is too small to be discriminating. Orthoesters in the D-*manno-* series can, however, easily be detected using the more crowded ^{1}H frequency region, but that is not the topic of this communication.

EXPERIMENTAL

General methods. NMR spectra were recorded at 25 °C for solutions in $CDCl_3$ using a JEOL GSX-270 spectrometer. The $^1J_{C\text{-}1,H\text{-}1}$ values were determined using a standard INEPT pulse sequence with no decoupling and 0.92 Hz digital resolution. The spectra were invariably in accordance with postulated structures. Concentrations were performed at reduced pressure at a bath temperature not exceeding 40 °C. Column chromatography was performed on silica gel (Matrex Silica Si 60A, 35-70 μ, Amicon). Yields were not subjected to optimization procedures. Elemental analyses were not performed.

In a typical reaction, DMTST[10] (1.4 mmol) was added at room temperature to a stirred mixture of the glycosyl donor (1.2 mmol) and the glycosyl acceptor (1.0 mmol) in dichloromethane (20 mL) containing 2,6-di-*tert*-butyl-4-methylpyridine (4.8 mmol) and ground molecular sieves (4Å) under nitrogen. When TLC indicated complete reaction, triethylamine (1 mL) was added and the reaction mixture was stirred for another 5 minutes. The mixture was diluted with toluene (20 mL), almost concentrated to dryness, and then chromatographed on silica gel.

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