crystallization from hexane gave yellow crystals with spectral features (NMR, IR, and mass) essentially identical with those reported by West.[11,12] When a solution of **2** was treated with methanol we obtained **3** in good yield. This compound was easily purified by column chromatography, and the assigned structure is supported by IR, NMR, and mass spectral data as well as elemental analyses. The addition of **2** to a THF solution of benzil gave a modest yield of the cycloaddition product **4**, a compound easily purified and characterized. IR, NMR, and mass spectral data and elemental analyses are consistent with the structure proposed for **4**. Analytically pure **3** and **4** were obtained in 72% and 38% yields, respectively, based on the quantity of **1**.

In a typical experiment, 1.5 mmol of **1** was added to a 100-mL round-bottomed single-necked flash containing 5 mL of dry THF (distilled from sodium benzophenone ketyl) and ≳3.0 mmol of lithium wire ($\sim^1/_4$ in. × 1/8 in. pieces) and partly submerged in a common ultrasound laboratory cleaner (117 V, 150 W, 50/60 Hz). After 20 min of sonication the yellow-orange product mixture was removed from the vessel by syringe and added to a warm solution of trapping agent.

For the methanol reaction the solution of **2** was added to excess dry methanol at 45 °C and maintained at this temperature for 30 min. The solvent and excess methanol were removed by flash evaporation, and methylene chloride was added. Filtration removed LiCl, and the product **3** was isolated by column chromatography (silica gel, 4:1 v/v pentane:CH_2Cl_2) to give 0.3 g (72%) of **3** as a pale yellow solid, mp 55–57 °C. The benzil quench was carried out in the same fashion by using a THF solution of excess benzil at 45 °C. The product, 1,2-diphenyl-4,4,5,5-tetramesityl-3,6-dioxo-4,5-disila-1-cyclohexene (**4**) was isolated as pale yellow crystals, mp 67–68 °C, following column chromatography.

The parallel between lithium-induced coupling reactions and electroreductive coupling reactions is obvious. In fact, a variety of chlorosilanes has been reduced to form disilanes by using constant-current electrolysis.[13] Dichlorosilanes give cyclopolysilanes under these conditions.[13] We have been investigating the electrosynthesis of polysilanes from chlorosilanes under controlled-potential conditions and have found that **1** produces **2** in a batch cell at −3.2 V vs. Ag/Ag^+.[14,15] We employed a 10-mL capacity, three-electrode divided cell with a mercury pool working electrode and a silver wire counter electrode. The electrolyte was tetrabutylammonium perchlorate dissolved in dimethoxyethane freshly distilled from sodium benzophenone ketyl. The half-wave potential of **1** was determined by differential pulse polarography at a dropping mercury electrode in the same solvent and found to be −2.8 V vs. Ag/Ag^+.

The amber product solution was treated with excess methanol, which discharged the color immediately. Removal of salts by crystallization was followed by column chromatography to give a 20% yield of analytically pure **2**. The reaction was carried out on 0.2 g of **1** at 40 mM.

We are investigating sonochemical and electrochemical routes to other novel organometallic species and will report our progress in due course.[16]

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Complete Analysis of Oligosaccharide Primary Structure Using Two-Dimensional High-Field Proton NMR

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The emerging importance of cell-surface glycolipids and glycoproteins in membrane function has stimulated interest in new methods for the elucidation of the primary structure of the oligosaccharide moieties of glyco-conjugates. The potential utility of proton NMR spectroscopy in obtaining this type of data was long ago recognized,[1a] since this method is sensitive, rapid, quantitative, and nondestructive. To date, one-dimensional proton NMR methods[2] have yielded fragmentary data concerning the primary structure of underivatized oligosaccharides. Two-dimensional (2-D) homo- and heteronuclear NMR methods have been used as an aid in the assignment of the proton spectrum of a disaccharide.[1b] However, no generally applicable and systematic method for the complete analysis of oligosaccharide primary structure has resulted, largely because of the severe resolution problems that result when nearly all resonances of such substances fall within a two-ppm chemical shift range and because of the tedium associated with sequential spin decoupling and nuclear Overhauser effect (NOE) experiments needed to establish connectivities within spectra. Two recent advances overcome these limitations, namely the introduction of very high-field NMR spectrometers (500 MHz) and 2-D homonuclear correlated NMR methods,[3-5] first applied to the analysis of polypeptide spectra by Ernst, Wüthrich, and co-workers.[3,5] We now illustrate the systematic application of these new methods to the complete structural analysis of an oligosaccharide, using the glycolipid gangliotriaosylceramide (**1**, Figure 1) as an example.

Glycolipid **1** (1.0 mg), obtained by desialylation[6] of ganglioside G_{M2} from human brain, was dissolved in dimethyl-d_6 sulfoxide, deuterium oxide (0.5 mL, 98:2 v/v; 1.8 mM). Two types of 2-D NMR experiments were performed on a 500 MHz Bruker WM-500 NMR spectrometer. The first experiment,[3,4] 2-D spin-echo correlation spectroscopy (SECSY), which establishes scalar coupling (J) connectivities between peaks, was executed by using two 90° pulses separated by a time $^1/_2t_1$. The first time domain was formed by incrementing t_1. FIDs acquired at the end of time t_1 provide the second time domain. The data are displayed as a contour plot. Except for small displacements due to J coupling,

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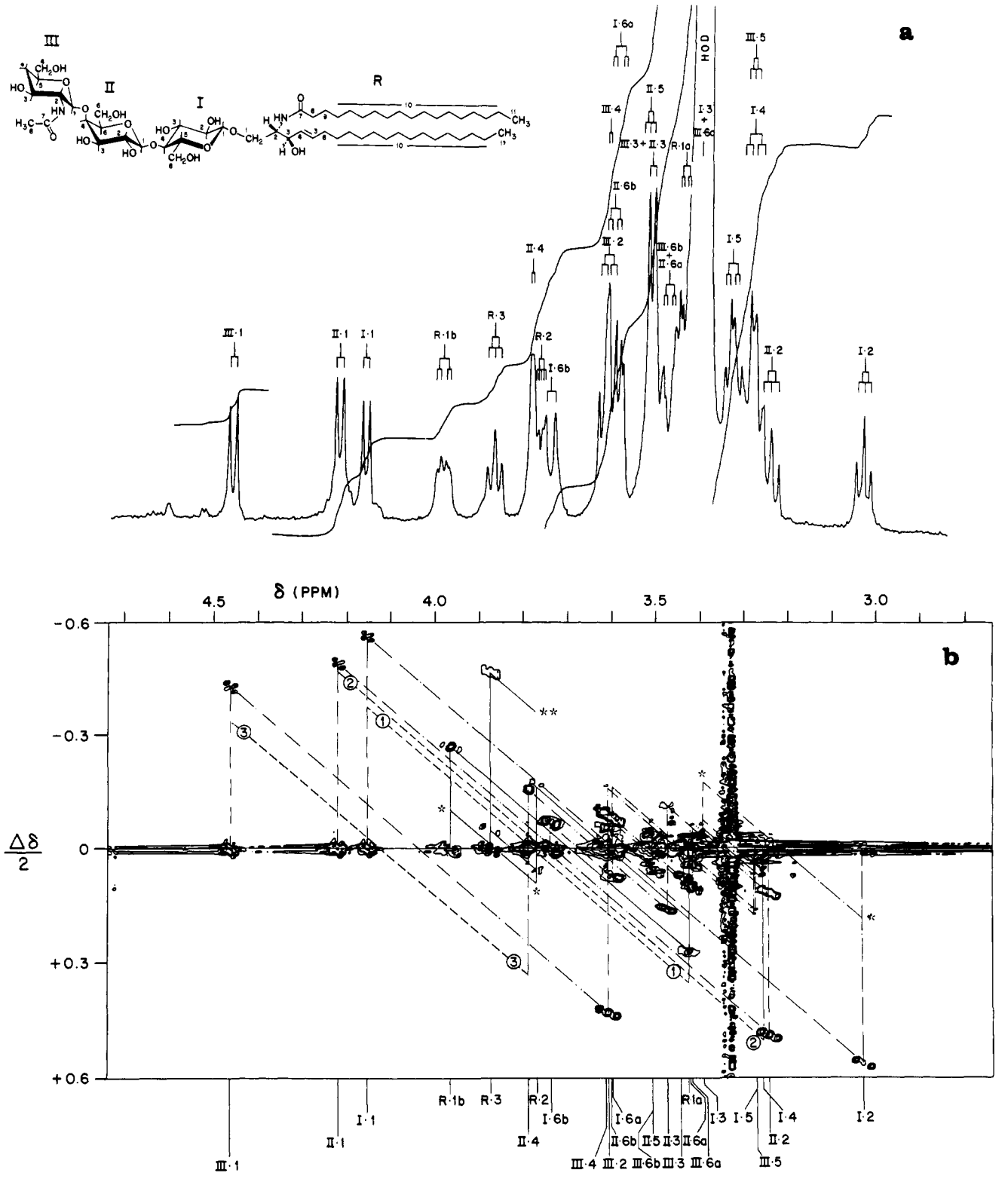

Figure 1. Structure and proton NMR spectra of gangliotriaosylceramide (**1**): (a) Integrated, one-dimensional spectrum of oligosaccharide ring proton region obtained at 30 °C, after 420 pulses in an 8K data set with a repetition rate of 10 s. Me_4Si was used as internal reference. (b) Two-dimensional SECSY spectrum obtained at 40 °C. A total of 16 pulses in a 256 × 1024 data set were required, taking approximately 2 h. *J* connectivities are labeled as follows: I, β-glucopyranosyl (–•–); II, β-galactopyranosyl (–••–); III, 2-acetamido-2-deoxy-β-galactopyranosyl (–•••–); R, ceramide (—). Also shown are the three (numbered) interresidue NOE couplings (– – –), obtained from the 2-D-NOE spectrum (which used 256 × 88 acquisitions and required 20.5 h). Other notations are for *J* connectivities observed at slightly lower contour thresholds (*) and to protons outside the observed window (**). A slight temperature dependence in chemical shift is to be noted, especially for the III-3 and II-3 resonances.

the central horizontal region corresponds to a normal 1-D spectrum and off-axis peaks occur at a vertical position corresponding to $^1/_2$ the chemical shift distance to a spin-coupled resonance. Sequential construction of vertical, 135°, and vertical lines identify coupled resonances. The data acquired for **1** and its analysis are presented in Figure 1b, along with the corresponding segment of a 1-D spectrum, Figure 1a.

The second experiment,[4,5] which establishes connectivities due to dipole–dipole cross relaxation (2-D-NOE), was executed by using a pair of 90° pulses separated by $^1/_2t_1$ to selectively invert

Table I. Proton Chemical Shifts (ppm) and Coupling Constants (Hz) for Gangliotriaosylceramide (1)[a]

residue	H-1 ($J_{1,2}$)	H-2 ($J_{2,3}$)	H-3 ($J_{3,4}$)	H-4 ($J_{4,5}$)	H-5 ($J_{5,6}$)	H-6 ($J_{6,6}$)	H-8
I	4.161[b] (7.8)	3.036 (8.2)	3.40[e] (8.8)	3.288[c] (10.3)	3.335[f](5.8, <1.5)	3.745, 3.598 (−10.8)	
II	4.222[c] (7.8)	3.245 (8.9)	3.519 (2.0)	3.789[d] (<1.5)	3.500 (5.0, 5.0)	3.604, 3.478 (−11.5)	
III	4.462[d] (8.4)	3.614 (10.0)	3.519 (2.5)	3.614 (<1.5)	3.293[f](6.3, 3.8)	3.478, 3.40[e] (−10.5)	1.884
R	3.442,[b] 3.987 (3.0, 3.9, $J_{1,1'}$ 9.3)	3.768 (7.8)	3.870 (7.4)	5.346 (15.2)	5.535 (7.3, 7.3)	1.932	2.021 ($J_{8,9}$ = 7.3)

[a] Obtained at 500 MHz and 30 °C in Me_2SO-d_6–D_2O (98:2, v/v), estimated error ±0.001 ppm and ±0.5 Hz. [b,c,d] Long-range, interresidue coupling demonstrated in 2-D-NOE spectrum. [e] Overlapped with HOD peak. [f] Assignments may be interchanged.

magnetization. Acquisition after a mixing delay, a third 90° pulse, and an additional delay of $^1/_2t_1$ is used to establish a second time domain, t_2. Mixing and pulse times were 0.5 s and 10 μs, respectively. Zero filling and a window function of $\cos^2$ (phase shifted by $\pi/4$) were used in both dimensions. Phase cycling and a small random increment added to the mixing delay were used to suppress J peaks. Processing and graphical identification of connected resonances is similar to that in the 2-D-SECSY experiment. 2-D-NOE data for **1** are included in Figure 1b and discussed below.

Spectral analysis begins by locating the oligosaccharide anomeric (H-1) protons in the 1-D spectrum, easily identified by their downfield chemical shifts (4.0–5.0 ppm) and single couplings. The anomeric region of **1** (Figure 1a) contains three doublets, indicating three aldose or aldoside residues are present, arbitrarily labeled I–III with increasing H-1 deshielding. The chemical shifts and large (>5 Hz) couplings of these protons indicate that each residue is β-pyranosidically linked. The equal intensity of these three doublets and the lack of an α-anomeric resonance confirm that none of the anomeric centers is free and mutarotating. Thus, **1** must be a trisaccharide β-glycosidically linked to an aglycone. The intense alkyl methyl and methylene resonances at 0.852 and 1.233 ppm, respectively, and the distinct subspectrum of the 2-acylamido-1,3-dihydroxy-4-alkenyl fragment[7] (R, Table I) indicate the aglycone is 1-O-linked ceramide.

Beginning with the anomeric resonances, three series of J connectivities are apparent in the 2D-SECSY spectrum (Figure 1b). With these connectivities and integration data as guides, all resonances of each residue of **1** are revealed and assigned (Table I). Each residue manifests a seven-spin AHMRV(XZ) system,[8] diagnostic of aldohexopyranoside rings. Due to the rigidity of such rings, imparted by chair conformations, and their known Karplus relationship,[9] the coupling constants observed between the five ring protons of each residue (Table I) dictate its stereochemistry. Thus, residue I has a *gluco* configuration, and II and III have a *galacto* configuration. The characteristic[2] downfield chemical shifts of H-1 and H-2 of residue III, but not I and II, indicate III is an *N*-acylhexosamine and I and II are hexoses. The three-proton singlet at 1.884 ppm indicates III is *N*-acetylated. Thus, I–III are, respectively, β-glucopyranosyl, β-galactopyranosyl, and 2-acetamido-2-deoxy-β-galactopyranosyl residues.[10] A J connectivity series is also seen for the ceramide (R) moiety (Figure 1b), confirming the aglycone assignment.

The oligosaccharide sequence and sites of glycosidic linkage are revealed through the 2-D-NOE spectrum. Inspection of the anomeric region reveals three through-space couplings for each anomeric proton, two of which are intraresidue 1,3 and 1,5 axial–axial couplings, used to confirm assignments. The third interresidue coupling observed for each anomeric proton is across the glycosidic linkage and, as noted in Figure 1b, between the following proton pairs: I-1 → R-1a, II-1 → I-4, and III-1 → II-4. Thus, the sequence of **1** must be III (1 → 4) II (1 → 4) I (1 → 1) R and its complete structure is 2-acetamido-2-deoxygalactopyranosyl (β-1 → 4) galactopyranosyl (β-1 → 4) glucopyranosyl (β-1 → 1) ceramide (Figure 1). This structure is in agreement with that assigned through chemical and enzymatic methods.[11]

It should be noted that the total time invested in these 2-D spectra is 23 h. While time consuming on a spectroscopy scale, this is very short compared to the many weeks required for convential chemical analysis.[12] Finally, we wish to report that since the above study of **1**, we have obtained 2-D-SECSY and 2-D-NOE spectra of four other oligosaccharides, including tetrasaccharides and pentasaccharides with branching structures and α-glycosidic linkages. In all cases a unique and correct primary structure was deduced. Complete analysis of the primary structure of an acetylated disaccharide using similar 2-D proton NMR methods has also been carried out recently in the laboratory of L. D. Hall (personal communication). Thus, the combination of 2-D, and high-field NMR promises to be a powerful new method for the rapid and nondestructive analysis of oligosaccharide primary structure.[13]

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Photosensitized [4 + 4] Cycloreversion of Anthracene Dimer via an Electron-Transfer Mechanism[1]

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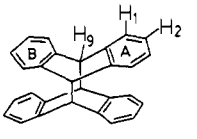
Although much attention has centered on photoinduced electron-transfer reactions in recent years, reports of cycloreversions proceeding by such a mechanism are exiguous and are restricted in [2 + 2] processes.[2] We report here the [4 + 4] cycloreversion of anthracene dimer **1** induced by electron-transfer sensitizers and provide evidence for the detailed mechanism.[3]



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