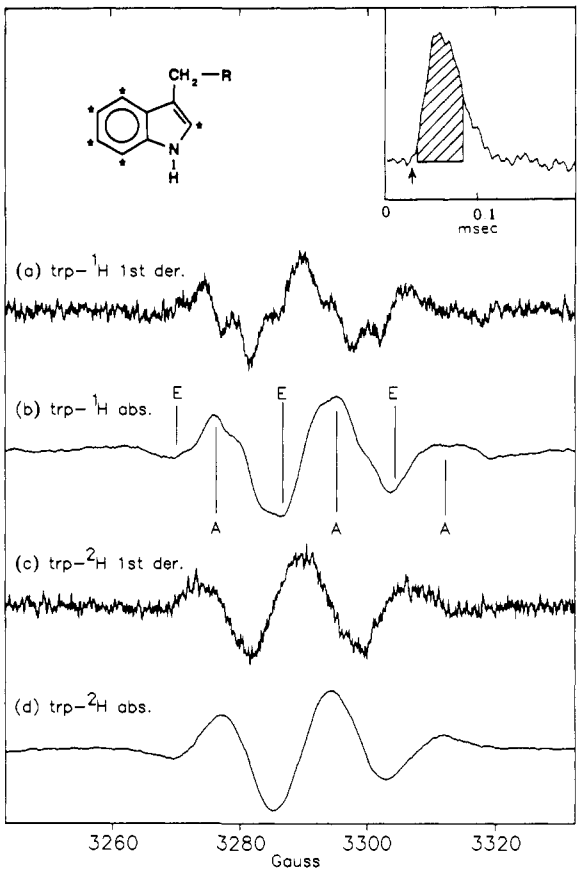

Figure 2. Time-resolved, first-derivative EPR spectra and the corresponding integrated spectra of the light-induced tryptophan radical in DNA photolyase. Spectrum a is the first-derivative spectrum of a protiated tryptophan sample. The field positions of emissive (E) and absorptive (A) peaks in the corresponding absorption spectrum were obtained by integrating the first-derivative spectrum in a to obtain the absorption spectrum b. Spectrum c is of a sample that contained tryptophan deuterated at the indole ring positions indicated by asterisks in the structure; d is the first integral of c. Instrument conditions were as in Figure 1. A 4-μs delay and a 48-μs aperture were used for the integration window. For a, five scans were averaged; this was increased to 20 scans for c. The inset shows the kinetic trace of the transient radical; the hatched area was integrated as a function of field to obtain the time-resolved spectrum.

of scans 4-fold produced a good-quality transient spectrum of the labeled species (Figure 2c). Comparison of the first-derivative spectra (Figure 2a,c) or of the first integrals (Figure 2b,d) shows that the partially resolved fine structure in the protiated enzyme is lost in the trp-d_5 sample. We conclude that the transient species arises from a tryptophan radical formed in the FADH$^\bullet$ reduction process.

The rapid decay of the spin-polarized signal is followed by less intense kinetic components. The amplitudes of these slower phases are field dependent and persist into the millisecond time regime.[6]

These results provide important insight into the mechanism of photoactivation of photolyase. Tryptophan involvement in this process[7] is confirmed here. Moreover, semiempirical MO calculations have indicated that significant hyperfine coupling to α-protons on the indole ring occurs for the cation radical but not for the neutral paramagnet.[12] These calculations, in conjunction with the labeling results in Figure 2, indicate that the trp radical occurs in its cation form, that is, the initial photoprocess involves electron transfer, not H atom transfer, from the indole side chain to the excited-state flavin. The implications of this conclusion for the photolyase thymine dimer repair mechanism will be presented in detail elsewhere.[3]

The observation of spin polarization in the photoactivation reaction is, at first glance, surprising, Previous work on this phenomenon has focused almost exclusively on either triplet precursors or doublet–doublet radical pairs.[13] The development of spin polarization through triplet–doublet splitting has been reported,[14] however, and studied recently in some detail.[15] In these cases, net emission or absorption is observed, and mechanisms that adapt aspects of the conventional triplet and radical pair mechanisms have been invoked to explain the observed polarization. The photolyase data here differ from these solution results as neither net emission nor absorption occurs; moreover, the extent of polarization is dependent upon hyperfine coupling, as shown by the data in Figure 2. These characteristics, as well as the polarization pattern observed in Figure 2b,d, are similar to the interacting CIDEP-correlated radical pair polarization (CRPP) case considered by Norris et al. for doublet–doublet spin polarization.[13] The fact that both the flavin triplet and tryptophan doublet are protein bound and are likely to remain interacting throughout the lifetime of the spin polarization suggests that an analogous CRPP mechanism[16] can be adapted to the triplet–doublet case that occurs in photolyase.[17]

Acknowledgment. This work was supported by NIH grants to A.S. (GM31082) and G.T.B. (GM37300). We thank Dr. Brian Hoffman for bringing the molecular orbital calculations on tryptophan radicals to our attention and Dr. Marion Thurnauer for discussions of doublet–triplet radical pair systems.

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A Novel Strategy for Synthesis of Ganglioside GM3 Using an Enzymatically Produced Sialoside Glycosyl Donor

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Received September 11, 1992

Synthesis of biologically important glycoconjugates by combined chemical and enzymatic methodologies is recognized as a promising practical approach.[1] The strategy of the combined synthesis has, to date, been limited to enzymatic glycosylation following chemical synthesis and deblocking of oligosaccharide precursors.[2] We report here an efficient synthesis of ganglioside GM3 using

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0002-7863/93/1515-1603$04.00/0

Table I. Kinetic Constants of **2**, **3**, and **4**

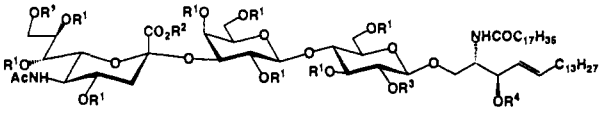
acceptor	Km (mM)	relative V_{max}	V_{max}/Km (mM^{-1})
2	0.8	1.3	1.6
3	9.8	1.4	0.15
4	1.6	1.0	0.63

a sialoside glycosyl donor prepared enzymatically. It is envisioned that a general strategy of using enzyme-assisted synthesis of suitable oligosaccharide glycosyl donors will extend the flexibility and utility of the combined chemical and enzymatic approach.

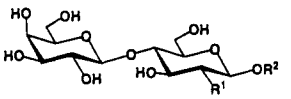
Several recent advances, such as cloning of glycosyltransferases,[3] development of cofactor regeneration systems,[4] and large-scale syntheses of nucleotide sugars,[5] have made the enzymatic approach an especially attractive alternative to the chemical glycosylation of certain problematic linkages. Chemical glycosylation, on the other hand, offers more flexibility in synthetic design and strategy. In addition, recent progress in the field of *O*-glycoside bond forming technology has made the strategy of block synthesis using oligosaccharides as glycosyl donors an accepted approach for the chemical synthesis of complex oligosaccharides.[6] Therefore, the use of glycosyltransferases[7] for syntheses of oligosaccharide glycosyl donors represents a powerful practical approach for complex glycoconjugates.

Such an approach is especially attractive for sialic acid (NeuAc) containing oligosaccharides (sialosides) because of the following reasons. First, NeuAc glycosides are the most difficult type of *O*-glycoside linkage to make chemically.[8] Second, NeuAc residues typically occur at the nonreducing end, affording an ideal situation for synthesis of appropriate sialoside glycosyl donor. Third, sialyltransferases, which possess distinct substrate specificities, have been cloned and are available as "recombinant" enzymes.[9]

Ganglioside GM3 (**1a**) has been used as a target for evaluation of a variety of synthetic methdologies.[10,11] This trisaccharide sequence (αNeuAc2→3βGal1→4βGlc) was synthesized previously from methyl lactoside and CMP-NeuAc[1a] by use of Galβ1→3/4GlcNAc α-2,3-sialyltransferase isolated from rat liver,[12] although in modest yield (30%). Since *N*-acetyllactosamine was previously recognized to be a better substrate than lactose, we investigated the 2-*O*-pivaloyl lactose derivative **2** as a substrate to take advantage of the well-recognized beneficial nature of bulky acyloxy group[13,14] for late-stage 1,2-trans glycosylation (with ceramide).



1a: $R^1=R^2=R^3=R^4=H$
1b: R^1=Ac, R^2=Me, R^3=$COCMe_3$, R^4=Bz

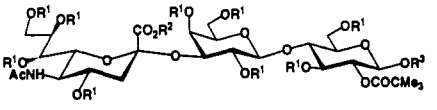


	R^1	R^2
2	$OCOCMe_3$	SE
3	OH	SE
4	NHAc	H

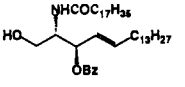
SE: $(CH_2)_2SiMe_3$

The relative reactivity of **2** was compared with those of simple lactoside **3** and *N*-acetyllactosamine (**4**) using recombinant βGal1→3/4GlcNAc α-2,3-sialyltransferase.[9c,15] As summarized in Table I, compound **2** proved to be a much better substrate than **3** and, surprisingly, even more reactive than **4**, which represents the disaccharide structure of the natural substrate on glycoprotein and glycolipid carbohydrate groups.

Preparative-scale sialylation of **2** was performed on the 0.2 mmol scale at 5 mM concentration, according to the CMP-NeuAc recycling protocol of Ichikawa et al.[4d,14] The product **5** (78% yield) was conveniently isolated by a column of *C*-18 reverse phase silica gel (Bio Rad), which was derivatized via **6** and **7** into the trichroloacetimidate **8**,[10d] in 78% overall yield.[14] Coupling with ceramide **9**[18,19] by the action of trimethylsilyl triflate (TMSOTf) afforded **1b** (72–76% yield).[14] Deprotection of **1b** gave ganglioside GM3 (**1a**) in quantitative yield.



	R^1	R^2	R^3
5	H	H	SE
6	Ac	Me	SE
7	Ac	Me	H (α, β)
8	Ac	Me	C(NH)CCl_3 (α, β)



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The combined chemical–enzymatic process described above afforded GM3 *in seven steps with 37% overall yield from NeuAc*, a substantial improvement in both ease of synthesis and overall yield compared to purely chemical synthesis.[10] Since large-scale preparation of both sialyltransferases[9] and CMP-NeuAc synthetase[4d,20] are now possible, the general methodology reported here, namely chemical conversion of suitable enzymatically pro-

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duced sialosides to glycosyl donors, should be widely applicable for the syntheses of various NeuAc-containing glycoconjugates.

Acknowledgment. This research was supported by grants from the NSF (DMB-88-21049) and NIH (GM-27904).

Supplementary Material Available: Experimental details for the synthesis of **2**, **3**, **6–8**, and **1b**, enzymatic sialylation of **2**, 300-MHz ^{1}H-NMR spectra of **5** and synthetic GM3, and Lineweaver–Burk plot for the determination of kinetic parameters (10 pages). Ordering information is given on any current masthead page.

Reaction of C_{60} with Silylene, the First Fullerene Silirane Derivative

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Received November 25, 1992

Since the isolation of Buckminsterfullerene (C_{60})[1] in preparatively useful quantities,[2] much attention has been devoted to its chemical reactivities[3] toward nucleophiles,[4] radicals,[5] reducing agents,[6] dienes,[4] dipoles,[4,7] zero-valent transition metals,[8] oxygen,[9] and also electrophiles.[10] Several functionalizations have been attempted, but only a few discrete individual products such as the

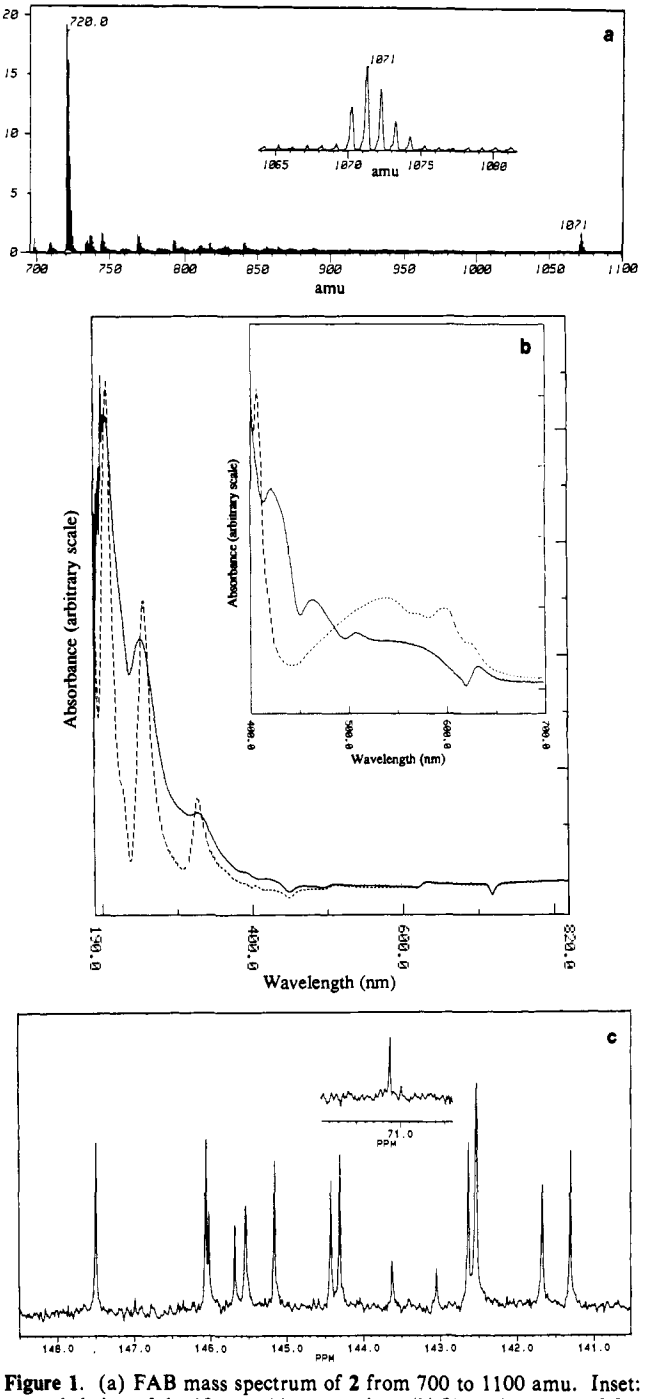

Figure 1. (a) FAB mass spectrum of **2** from 700 to 1100 amu. Inset: expanded view of the 1065–1080-amu region. (b) UV–Vis spectra of C_{60} (---) and **2** (—) from 400 to 700 nm in toluene. Inset: spectra of C_{60} (---) and **2** (—) from 190 to 829 nm in hexane. (c) ^{13}C NMR spectrum of **2**.

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