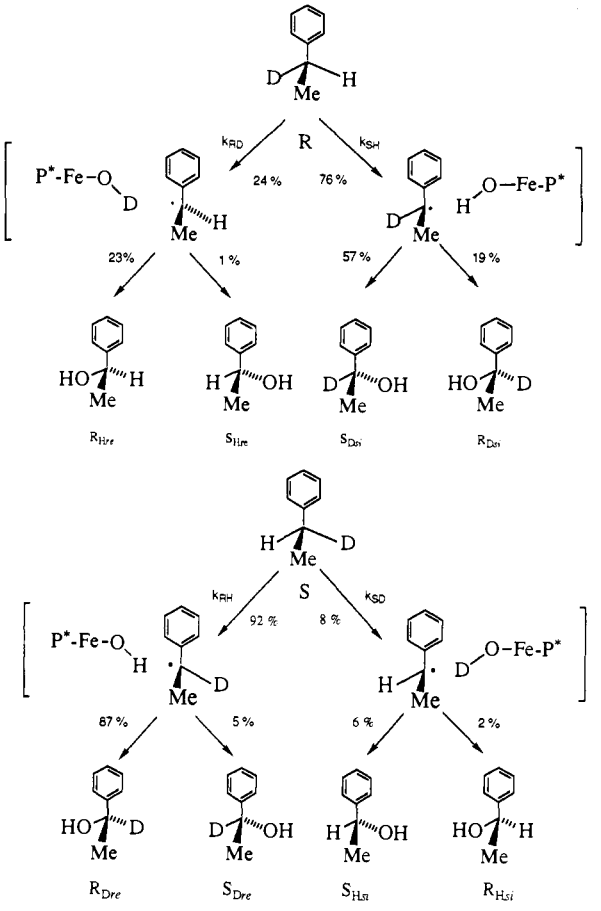
Table I. Mass Spectral Data for 1-Phenylethyl Esters Derived from (*R*)- and (*S*)-(1-Deuterioethyl)benzene[a]

	substrate				esters[b] from	
	(*R*)-ethyl-*1-d*-benzene		(*S*)-ethyl-*1-d*-benzene			
m/z	*R,R* ester rel int, %	*R,S* ester rel int, %	*R,R* ester rel int, %	*R,S* ester rel int, %	1-phenylethanol rel int, %	1-phenylethan-*1-d*-ol rel int, %
253	1.75	0.82	0.77	4.72	1.12	0.9
254	98.56	3.51	1.8	85.01	100.0	1.75
255	100.0	100.0	100.0	100.0	19.12	100.0
256	19.3	19.92	19.87	19.78	0.4	16.5
rel yield, %	42	58	88	12		
% deuterated	45.7	98.3	99.0	49.6	0.0	100.0
% ee	16		77			

[a] The relative intensities are averaged over the GC peak and are uncorrected. Deuterium percentages are corrected for ^{13}C natural abundance. Determinations of at least three oxidations were reproducible to ±2%. [b] These authentic phenylethyl esters were made from racemic alcohols.

Scheme II



amounts of hydrogen and deuterium.

Analysis of the results is simplified by consideration of the stepwise hydroxylation process outlined in Scheme II. The C–H bond scission and subsequent C–O bond formation are stereochemically discrete events.[4,9] The intrinsic stereoselectivity for hydrogen removal from ethylbenzene by **1** can be derived from the observed ratio of *R* and *S* alcohols (71:29), and the stereoselectivity of the capture of the intermediate becomes $k_{RH}/k_{SH} = 2.0$, where the subscript RH indicates *hydrogen* removal from the *pro-R* position. The deuterium inventory also allows a direct measure of the ratios $k_{RD}/k_{SH} = 0.311$ and $k_{RH}/k_{SD} = 12.7$ and, as indicated in eq 1, an independent measure of the isotope effects for H(D) removal from the *R* and *S* positions. The equivalence of these two values (6.4) is reassuring and the magnitude in accord with the intramolecular isotope effect for ethylbenzene-d_{10} ($k_H/k_D = 8.7$), which should be inflated by secondary isotope effects and a higher degree of deuteration.

$$k_{RH}/k_{RD} = \frac{k_{RH}/k_{SH}}{k_{RD}/k_{SH}} = 6.4 = \frac{k_{SH}/k_{RH}}{k_{SD}/k_{RH}} = k_{SH}/k_{SD} \quad (1)$$

The results indicate that the chiral porphyrin catalyst **1** has a 2-fold preference for removal of the *pro-R* hydrogen of ethylbenzene. More significantly, however, it is apparent that the radical produced by removal of either H or D from the *pro-R* site is captured with nearly complete *retention* of configuration whereas 20–25% *inversion* (40–50% racemization) results from H(D) removal from the *pro-S* position. Accordingly, by the usual criteria of mechanism, the enantiotopic protons of ethylbenzene are hydroxylated by **1** *by different mechanisms.*

A more satisfying interpretation is that the same mechanism, hydrogen abstraction and subsequent geminate cage recombination,[20] occurs in both cases. Capture of the incipient carbon radical must occur rapidly on the preferred *re* face due to the good fit of the substrate into the binaphthyl cavity. By contrast, the unfavorable nonbonded interactions encountered by the radical on the *si* face afford an opportunity for significant racemization. The results described here for this simple model system provide a clear indication as to how it is possible for asymmetric catalyst–substrate interactions to impose stereoselectivity on a free-radical reaction.

Acknowledgment. Support for this research by the National Institutes of Health (GM-36298) is gratefully acknowledged. The National Science Foundation and the NIH provided funds for the purchase of a high-resolution mass spectrometer.

(20) Greene, F. D. *J. Am. Chem. Soc.* **1955**, *77*, 4869.

Spectroscopic Detection of Organolanthanide Dihydrogen and Olefin Complexes

Steven P. Nolan and Tobin J. Marks*

Department of Chemistry, Northwestern University Evanston, Illinois 60208-3113

Received July 3, 1989

Although dihydrogen complexes[1,2] (**1**) are frequently invoked along the reaction coordinate for lanthanide-centered, actinide-

(1) (a) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 126–128. (b) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299–337 and references therein. (c) Kubas, G. J. *Comments Inorg. Chem.* **1988**, *7*, 17–40 and references therein.

(2) (a) Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1989**, *28*, 6–8. (b) Gonzalez, A. A.; Zhang, K.; Nolan, S. P.; Lopez de la Vega, R.; Mukerjee, S. L.; Hoff, C. D.; Kubas, G. J. *Organometallics* **1988**, *7*, 2429–2435. (c) Bautista, M. F.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Sella, A. *J. Am. Chem. Soc.* **1988**, *110*, 7031–7036. (d) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865–5867. (e) Bianchini, C.; Mealli, C.; Peruzzini, M.; Zandini, F. *J. Am. Chem. Soc.* **1987**, *109*, 5548–5549.

0002-7863/89/1511-8538$01.50/0

$$Cp'_2Eu + H_2 \rightleftharpoons Cp'_2Eu \cdot H_2$$

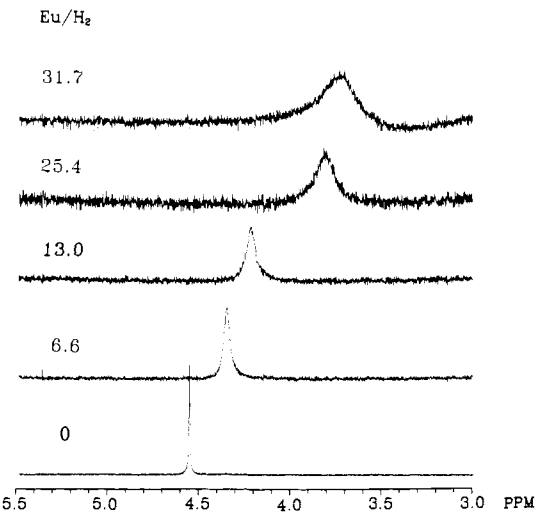
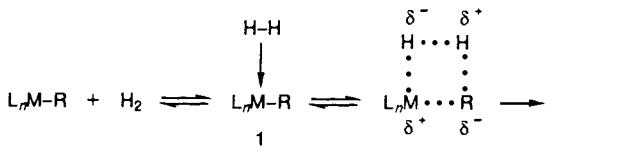


Figure 1. ^1H NMR spectra (400 MHz) of a 9.0 mM H_2 solution in C_6D_{12} containing the indicated equivalents of Cp'_2Eu.

centered, and d^0 transition element-centered hydrogenolytic processes (e.g., **1**, eq 1),[3,4] the existence of such species remains



(1)

highly speculative. A significant question concerns the viability of metal-dihydrogen coordination at an electron-deficient center not likely to engage in extensive, perhaps requisite, metal → $H_2(\sigma^*)$ backbonding.[1,2,5] We report here[6] the first spectroscopic detection of an organolanthanide dihydrogen complex utilizing a coordinatively unsaturated, paramagnetic NMR probe selected for high sensitivity to complexation and thermodynamic unfavorability of oxidative addition[7] or metal-ligand bond hydrogenolysis.

$$Cp'_2Eu + \| \rightleftharpoons Cp'_2Eu \cdot \|$$

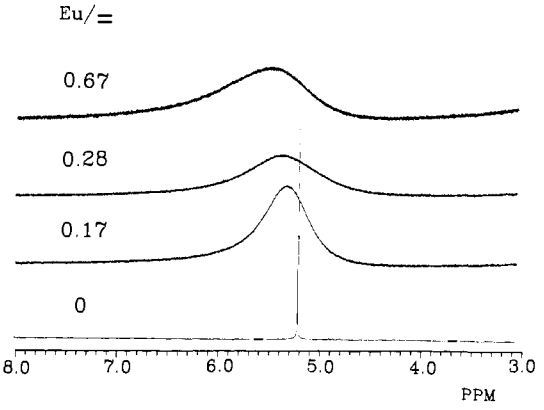
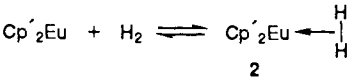


Figure 2. ^1H NMR spectra (400 MHz) of a 40.0 mM ethylene solution in C_6D_{12} containing the indicated equivalents of Cp'_2Eu.

Incremental addition of Cp'_2Eu ($Cp' = \eta^5$-$(CH_3)_5C_5$)[8] to a C_6D_{12} solution of H_2 at constant $[H_2]$ results in upfield displacement (vs internal $C_6D_{11}H$) and pronounced broadening of the dissolved H_2 resonance (Figure 1). We interpret this behavior in terms of eq 2, where ligand exchange is rapid on the NMR time



(2)

scale (down to −85 °C in $C_6D_{11}CD_3$) and where large unpaired spin delocalization shifts, minimal dipolar shifts, and slow electronic spin-lattice relaxation (extensive spectral broadening) are normally expected in a $4f^7$ ($^8S_{7/2}$, $\langle S_Z \rangle_J \approx -31.5$) system.[9] Structure **2** is proposed on the basis of theory[4,10] and analogy to H_3^+.[11] The direction of the paramagnetic shift is that expected for a $4f^7$ system with unpaired spin density delocalized predominantly via a polarization mechanism.[9,12] Addition of THF-d_8 to these solutions displaces the H_2 resonance toward the uncomplexed position, indicating competition for the acidic europium center.

Equation 2 raises the question of whether complexation (in competition with C_6D_{12}) might also be observed for hydrocarbons of sufficient basicity.[11c] Lanthanide-, actinide-, and d^0-olefin complexes are frequently invoked along pathways for insertion processes,[3b,g,13,14] and Figure 2 indicates that Cp'_2Eu-ethylene

(3) (a) Lin, Z.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 7979–7985. (b) Thompson, M. R.; Baxter, S. M.; Bulls, A. R.; Burber, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203–219. (c) Jordan, R. F.; Bajgur, C. S.; Dasher, W. E.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1041–1051. (d) Wochner, F.; Brintzinger, H. H. *J. Organomet. Chem.* **1986**, *309*, 65–75. (e) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111–8118. (f) Gell, K. I.; Posin, B.; Schwartz, J.; Williams, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1846–1855. (g) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650–6667.

(4) For relevant theoretical studies, see: (a) Rabaâ, H.; Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1986**, *108*, 4327–4333 and references therein. (b) Steigerwald, M. L.; Goddard, W. A., III *J. Am. Chem. Soc.* **1984**, *106*, 308–311. (c) Brintzinger, H. H. *J. Organomet. Chem.* **1979**, *171*, 337–348.

(5) (a) Hay, P. J. *J. Am. Chem. Soc.* **1987**, *109*, 705–710. (b) Jean, Y.; Lledos, A. *Nouv. J. Chim.* **1987**, *11*, 651–656. (c) Burdett, J. K.; Phillips, J. R.; Pourian, M. R.; Poliakoff, M.; Turner, J. J.; Upmacis, R. *Inorg. Chem.* **1987**, *26*, 3054–3063. (d) Jean, Y.; Eisenstein, O.; Volatron, F.; Maouche, B.; Sefta, F. *J. Am. Chem. Soc.* **1986**, *108*, 6587–6592.

(6) Communicated in part: Marks, T. J. *Abstracts of Papers*, 197th National Meeting of the American Chemical Society, Dallas, TX, April 9–14, 1989; American Chemical Society: Washington, DC, 1989; INOR 8.

(7) (a) Bond enthalpy data[7a–d] argue that $2Cp'_2Eu + H_2 \rightarrow (Cp'_2EuH)_2$ is endergonic by $>+15$ kcal mol^{-1}. (b) Nolan, S. P.; Stern, D.; Marks, T. J. *J. Am. Chem. Soc.*, in press. (c) Nolan, S. P.; Stern, D.; Marks, T. J. *Abstracts of Papers*, 196th National Meeting of the American Chemical Society, Los Angeles, CA, Sept. 25–30, 1988; American Chemical Society: Washington, DC, 1988; INOR 378. (d) Nolan, S. P.; Stern, D.; Marks, T. J., manuscript in preparation.

(8) (a) Evans, W. J.; Hughes, L. A.; Hanusa, T. J. *Organometallics* **1986**, *5*, 1285–1291. (b) Tilley, T. D.; Andersen, R. A.; Spencer, B.; Ruben, H.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1980**, *19*, 2999–3003. (c) All manipulations were carried out by using rigorously anaerobic vacuum line and glove box techniques. Solution concentrations were calibrated independently by using ferrocene as an internal standard.

(9) (a) Gamp, E.; Shimomoto, R.; Edelstein, N.; McGarvey, B. R. *Inorg. Chem.* **1987**, *26*, 2177–2782 and references therein. (b) Bertini, I.; Luchinat, C. *NMR of Paramagnetic Molecules in Biological Systems*; Benjamin: Menlo Park, CA, 1986; Chapter 10. (c) Fischer, R. D. In *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fragalá, I. L., Eds.; Reidel: Dordrecht, 1985; Chapter 8. (d) McGarvey, B. R. In *Organometallics of the f-Elements*; Marks, T. J., Fischer, R. D., Eds.; Reidel Publishing Co.: Dordrecht, 1979; Chapter 10. (e) Fischer, R. D. *Ibid.*; Chapter 11.

(10) The EHMO-derived potential for Cp'_2(lanthanide)←(η^2-RH) interactions is "soft" (Tatsumi, K., private communication).

(11) (a) Oka, T. *Phys. Rev. Lett.* **1980**, *45*, 531–534. (b) Gaillard, M. J., et al. *Phys. Rev. A* **1978**, *16*, 1686–1793. (c) The proton affinity of H_2 is 101 kcal mol^{-1}: Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695–808.

(12) (a) Reference 9b, Chapter 2. (b) McGarvey, B. R. *Can. J. Chem.* **1984**, *62*, 1349–1355. (c) McGarvey, B. R. *J. Chem. Phys.* **1976**, *65*, 955–961. (d) Luke, W. D.; Streitwieser, A., Jr. *ACS Symp. Ser.* **1980**, *131*, 93–140. (e) Marks, T. J.; Kolb, J. R. *J. Am. Chem. Soc.* **1975**, *97*, 27–35. (f) Horrocks, W. DeW., Jr. In *NMR of Paramagnetic Molecules*; La Mar, G. N., Horrocks, W. DeW., Jr., Holm, R. H., Eds.; Academic Press: New York, 1973; Chapter 4.

(13) (a) Evans, W. J. *Polyhedron* **1987**, *6*, 803–835. (b) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091–8103. (c) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51–56.

coordination can also be detected (eq 3). That the paramagnetic

$$Cp'_2Eu + \| \rightleftharpoons Cp'_2Eu \leftarrow \| \quad (3)$$

shift direction (*downfield*) of the olefinic protons is opposite to that observed in H_2 is in accord with complexation of the olefin π system and delocalization through the ligand framework of polarization-derived, carbon-centered unpaired spin density.[12] The opposite, *upfield* displacement of the methyl signal in an analogous experiment with propylene is further support for this mechanism.[12] In regard to saturated hydrocarbons, negligible preferential interaction is observed between Cp'_2Eu and methane. However, in the case of more basic[11c] cyclopropane, substantial broadening and upfield displacement of the hydrocarbon ^1H signal is observed.[15]

Efforts to extract[16] accurate bound shift (Δ) and binding constant (K) information from shift/stoichiometry data are complicated by the large line widths and limitations in solubility. A preliminary analysis[17] indicates that $\Delta/K \approx 1$ for eq 1 and 2, which, in view of the large anticipated values of Δ,[12] implies small binding constants. Further studies are in progress.

Acknowledgment. We are grateful to the NSF for support of this research under Grant CHE-8800813.

(14) $Cp'_2Yb(\mu\text{-}C_2H_4)Pt(PPh_3)_2$ is isolable as a solid, but significantly dissociated into Cp'_2Yb and $(C_2H_4)Pt(PPh_3)_2$ in solution: Burns, C. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 915-917.

(15) For comparable concentrations, paramagnetic shifts are roughly comparable to those observed for $Cp'_2Eu + H_2$.

(16) (a) Reference 9b, Chapter 4. (b) Inagaki, F.; Miyazawa, T. *Prog. Nucl. Magn. Reson. Spectrosc.* **1981**, *14*, 67-111. (c) Inagaki, F.; Miyazawa, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1427-1430. (d) Shapiro, B. L.; Johnston, M. D., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 8185-8191.

(17) Least-squares analysis of $1/\Delta$ vs $1/[Eu]$ data at constant concentration of substrate assuming 1:1 complexes.

n-Pentenyl Glycosides Facilitate a Stereoselective Synthesis of the Pentasaccharide Core of the Protein Membrane Anchor Found in *Trypanosoma brucei*[1]

David R. Mootoo,[2] Peter Konradsson, and Bert Fraser-Reid*

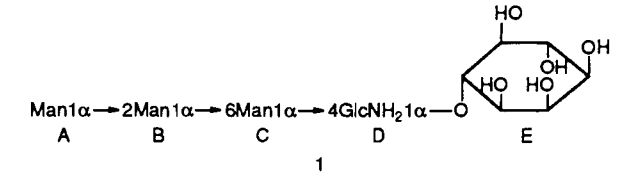
Department of Chemistry
Paul M. Gross Chemical Laboratory
Duke University
Durham, North Carolina 27706

Received June 9, 1989

Recent investigations in this laboratory have revealed that *n*-pentenyl glycosides (NPGs) offer some remarkable advantages for processes that require activation of the anomeric center of sugars. Glycosyl donors commonly in use[3] may possess one or another of the following attributes, but NPGs are unique in that they possess all seven: (1) direct preparation from an aldose by modified Fischer glycosidation procedures,[4] (2) stability to diverse chemical manipulations and compatibility with standard protecting groups,[4a,5] (3) mild, chemospecific, and nontoxic activation of the anomeric center,[4-6] (4) direct use in saccharide coupling,[5-7] (5) control of the α,β selectivity in glycosidation by choice of solvent,[5] and by other methods,[6,8] (6) ready conversion into glycosyl halides for Koenigs-Knorr reactions,[9] and (7) *most uniquely, the ability to "arm" or "disarm" these glycosyl donors by means of the protecting group on the C2 oxygen.*[7]

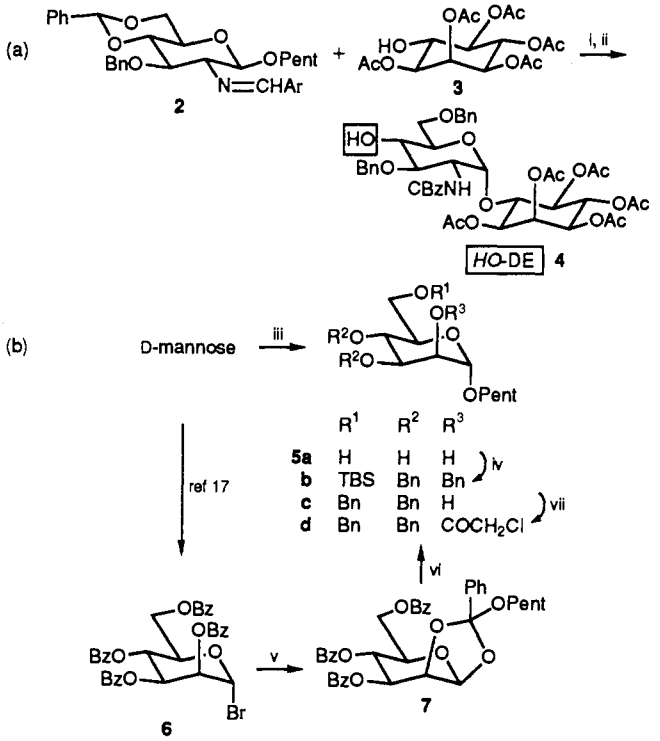
These attributes offer much promise for meeting the daunting demands of oligosaccharide syntheses,[3,10] and as an appropriate testing ground, we have addressed the synthesis of the mannan-rich pentasaccharide **1** from the core oligosaccharide of the variant surface glycoprotein[11] found in *Trypanosoma brucei*[12,13] (Scheme

Scheme I



1

Scheme II[a]



[a] (i) $I(collidine)_2ClO_4/CH_2Cl_2$/4A molecular sieves, then 10% MeOH in HOAc/$TsNHNH_2$/room temperature, then $Et_3N/CBzCl$/0 °C, 65%; (ii) $NaBH_3(CN)/THF\text{-}Et_2O/HCl$/4A molecular sieves, 75%; (iii) $CH_2{=}CH(CH_2)_3OH$/DMSO/camphorsulfonic acid/90 °C/24 h,[3] 65%; (iv) *tert*-butyldiphenylsilyl chloride/Et_3N/DMAP/CH_2Cl_2, then $PhCH_2Br/NaH$, DMF, 62%; (v) $CH_2{=}CH(CH_2)_3OH$/lutidine/CH_2Cl_2, 90%; (vi) NaOMe, then $PhCH_2Br/NaH$/DMF, then camphorsulfonic acid/CH_2Cl_2, 64%; (vii) $(ClCH_2CO)_2O$/pyridine, 65%.

(1) We are gratetul to the National Science Foundation (CHE 8703916) and Glaxo Laboratories, Inc. (Durham, NC), for financial support of this work.

(2) Present address: Department of Chemistry, CUNY, Hunter College, 695 Park Avenue, New York, NY 10021.

(3) (a) Paulsen, H. *Angew. Chem., Int. Ed. Engl.* **1982**, 144. (b) Schmidt, R. R. *Angew. Chem., Int. Ed. Engl.* **1986**, 212. (c) Fugedi, P.; Garegg, P. J.; Lonn, H.; Norberg, T. *Glycoconjugat J.* **1987**, *4*, 97. (d) Nicolaou, K. C.; Randall, J. L.; Furst, G. T. *J. Am. Chem. Soc.* **1985**, *107*, 5556. (e) Fugedi, P.; Birberg, W.; Garegg, P. J.; Pilotti, A. *Carbohydr. Res.* **1987**, *164*, 297. (f) Sadozai, K. K.; Nukada, T.; Ito, Y.; Nakahava, Y.; Ogawa, T.; Kobata, A. *Carbohydr. Res.* **1986**, *157*, 101.

(4) (a) Mootoo, D. R.; Date, V.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1988**, *110*, 2662. (b) Konradsson, P.; Fraser-Reid, unpublished results.

(5) Fraser-Reid, B.; Konradsson, P.; Mootoo, D. R.; Udodong, U. *J. Chem. Soc., Chem. Commun.* **1988**, 823.

(6) The use of *N*-iodosuccinimide and trifluoromethanesulfonic acid (NIS/TfOH) as a source of iodonium ions has been developed in this laboratory. The details, which will be published elsewhere, are available in the supplementary material.

(7) Mootoo, D. R.; Konradsson, P.; Udodong, U.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1988**, *110*, 5582.

(8) Mootoo, D. R.; Fraser-Reid, B. *Tetrahedron Lett.* **1989**, *30*, 2363.

(9) Konradsson, P.; Fraser-Reid, B. *J. Chem. Soc., Chem. Commun.*, in press.

(10) Lemieux, R. U. *Chem. Soc. Rev.* **1978**, *7*, 432.

(11) These intriguing substances reveal a novel mechanism for how proteins are anchored to cell membranes and hence are thought to be implicated in signal transduction. For example, see: (a) Schmitz, B.; Klein, R. A.; Duncan, I. A.; Egge, H.; Gunawan, J.; Peter-Katalinic, J.; Dabrowski, Y.; Dabrowski, J. *Biochem. Biophys. Res. Commun.* **1987**, *146*, 1055. (b) Cross, G. A. M. *Cell* **1987**, *48*, 179. (c) Low, M. G. *Biochem. J.* **1987**, *244*, 1. (d) Saltiel, A. R.; Cuatrecasas *Am. J. Physiol.* **1988**, *255*, C1.

0002-7863/89/1511-8540$01.50/0