cessity for a Brönsted acid in these model processes is particularly noteworthy since both the source and role of Brönsted acid sites on the surface catalysts have been the subject of considerable speculation.[11] The facile S-H additions in the systems presented here also suggest intriguing mechanistic possibilities for the reduction of nitriles and other substrates of nitrogenase, in which a sulfido-bridged molybdenum iron cluster is proposed as the active site.[12]

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Supplementary Material Available: Crystal data and details of the structural determination and tables of bond distances, bond angles, and atomic and thermal parameters for $[(CpMo)_2(S_2CH_2)(S_2CCH_3)]Br\cdot{}^1/_2EtOH$ and characterization data for cationic molybdenum derivatives (10 page); table of observed and calculated structure factors for $[(CpMo)_2(S_2CH_2)(S_2CCH_3)]Br\cdot{}^1/_2EtOH$ (32 pages). Ordering information is given on any current masthead page.

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[4 + 2] Cycloaddition of Azodicarboxylate and Glycals: A Novel and Simple Method for the Preparation of 2-Amino-2-deoxy Carbohydrates

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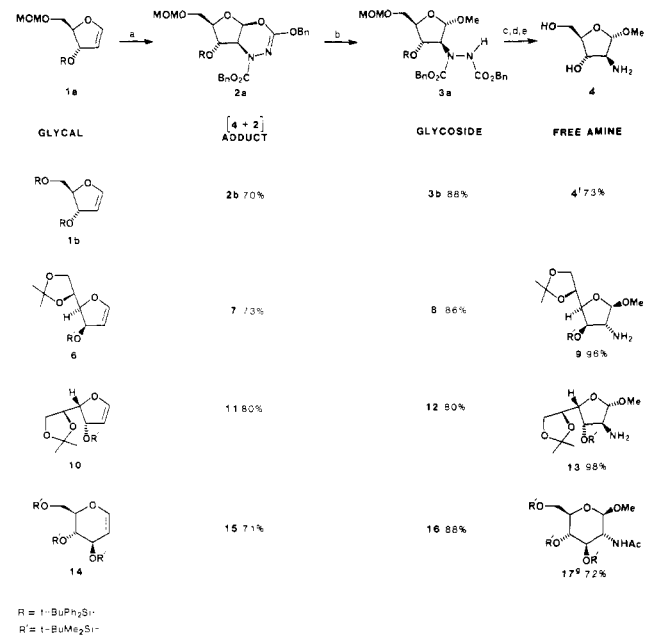
The amino sugars are an important group of natural products. These molecules are widely distributed in nature, being found in almost all living creatures, and play diverse biologically important roles. While the amino sugar is often part of a larger molecule, its presence is usually important to the biological function. Examples of important molecules containing amino sugars are aminosaccharide antibiotics,[1] antigenic determinants,[2] glycoproteins, and glycolipids.[3]

Despite their ubiquitous nature, few methods exist for the preparation of amino sugars. The most stereoselective method for the synthesis of amino sugars is a SN_2 displacement of an epoxide or sulfonate ester by azide or ammonia.[4] However, this reaction requires selective derivatization and in the sulfonate ester case is often not possible at C-2. An amino group may also be introduced by reduction of carbon-nitrogen double bond[5] or by oxy-amination of a double bond.[6-8] These methods, while being widely used, can lead to stereo- and/or regioisomers. Therefore a method which would allow the stereo- and regioselective introduction of a nitrogen to a carbohydrate derivative leading to only one amino sugar would be of considerable utility.

Herein we report a novel, simple, and mild method for the stereoselective introduction of a nitrogen functionality and the subsequent transformation of the products of this reaction into 2-amino glycosides. The cycloaddition of azodicarboxylates on simple vinyl ethers was first reported in 1969[9] to give [4 + 2] and/or [2 + 2] adducts, depending on the substrate. This reaction was thoroughly studied from a mechanistic point of view on simple substrates. For this reaction to be synthetically useful a high diastereoselectivity would be desirable. It was felt that this diastereoselectivity would be most readily attainable with a rigid substrate having an appropriately placed substituent, such as an allylically substituted cyclic vinyl ether. Carbohydrate-derived glycals meet these criteria well, since a stereoselective cycloaddition between an azodicarboxylate and a glycal would give a convenient method to introduce an amino function at C-2 of a carbohydrate. This approach was taken to explore the synthetic utility of this reaction.

The glycals **1a**, **6**, and **10** were prepared by the procedure of Ireland et al.[10] The glycal **1b** was prepared by dehydration of 3,5-di-*O*-(*tert*-butyldiphenylsilyl)-2-deoxy-D-ribofuranose (**5**)[11,12]

Scheme I[a]



[a] (a) $BnO_2C-N=N-CO_2Bn$, cyclohexane, CH_2Cl_2, 350 nm, 18 h (73%); (b) *p*-TSOH·H_2O, MeOH (95%); (c) Raney Ni, W-2, H_2 40PSI, MeOH-AcOH (60:1) (80%); (d) *n*-Bu_4NF, THF (95%); (e) AcCl, MeOH (4 N HCl) (95%); (f) the hydrogenolysis was performed on the free diol obtained by desilylation of compound **3b** (*n*-Bu_4NF 10 equiv AcOH 3 equiv THF, 90%); (g) The free amine was converted to its *N*-acetate by treatment with acetic anhydride.

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(12) The lactol **5** was prepared starting from the methyl 2-deoxy-D-ribofuranoside. The diol was protected as its bis(*tert*-butyldiphenylsilyl ether). Subsequent hydrolysis of the methyl furanoside using a mixture of ACOH/THF/H_2O (7:2:2) at 65 °C for 6 h gave the lactol **5**.

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with the Mukaiyama reagent.[13] Irradiation at 350 nm for 18 h of a solution of the glycal **1a** and 5 equiv of dibenzyl azodicarboxylate (DBAD)[14] in cyclohexane gave a single [4 + 2] cycloadduct **2a** (TLC, ^{1}H NMR, HPLC) in 73% yield (Scheme I) (for a typical procedure see ref 15). Glycals **1b**, **6**, **10**, and **14** could be converted into their corresponding cycloadducts (**2b**, **7**, **11**, **15**) in similar yields (Scheme I).

The diastereofacial selectivity of the cycloaddition is apparently controlled by the stereochemistry at C-3 and was assigned on the basis of NOE studies and by conversion of the adducts **2a**, **2b**, **7**, and **15** into known compounds. That the product was a [4 + 2] cycloadduct vs. a [2 + 2] was confirmed by the presence of the characteristic C=N band of dihydrooxadiazines in the IR spectra (~1670 cm^{-1}).[9]

Treatment of the cycloadducts with a catalytic amount of *p*-toluene sulfonic acid in methanol gave the corresponding methyl glycosides (**3a**, **3b**, **8**, **12**, **16**) in quantitative yield. The opening of the cycloadducts by methanol occurred exclusively with inversion at C-1.[17] Hydrogenolysis of the protected hydrazines gave the 2-amino glycosides (**4**, **9**, **13**, **17**) in high yields (Scheme I). Manipulation of the protecting groups of the amines **4**, **9**, and **17** gave cited compounds which possessed identical characteristics (^{1}H NMR, mp, $[\alpha]_D$) with those reported in the literature,[17-22] thus confirming the stereochemical assignments made on the basis of NOE data. The amino furanoside **13** is a derivative of the hereto unreported methyl 2-amino-2-deoxy-α-D-idofuranoside.

There are several features of the transformations described above that bear comment. Substitution of water for methanol in opening of the cycloadduct would yield the lactol which could be further transformed via its aldehyde and/or hydroxyl moieties. Also noteworthy is that the nitrogen functionality is obtained directly in a protected form obviating the need for protection if one wishes to use the product as a synthetic intermediate.

In summary, 2-deoxy-2-amino glycosides can be prepared simply and in high yield by the cycloaddition of DBAD on the appropriate glycal. Due to the simplicity and mildness of the reaction conditions this reaction should be readily extendable to non-carbohydrate cases. Such studies are currently under way and will be reported in due course.

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Supplementary Material Available: Analytical and spectral data for **4**, **7-9**, **13**, and **18** (4 pages). Ordering information given on any current masthead page.

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(15) To a solution of **1a** (417 mg, 1.5 mmol) in cyclohexane (3 mL) was added the DBAD (2.26 g, 7.58 mmol, 5 equiv). The suspension was solubilized by the addition of CH_2Cl_2 (approximately 500 μL) and then irradiated at 350 nm (approximately 18 h). Evaporation and subsequent flash chromatography (30% ether in hexanes) gave 638 mg (73%) of the cycloadduct **2a** (R_f = 0.4 40% ether in hexanes, $[\alpha]^{22}_D$ +106.6° (*c* 1.3, $CHCl_3$)).
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(21) Methyl 2-amino-2-deoxy-5,6-*O*-(1-methylethylidene)-β-D-glucofuranoside (**18**) (supplementary material) as a white solid; mp 60 °C (ether), $[\alpha]^{22}_D$ -58.8° (*c* 0.4, methanol); lit.[17] mp 61-62 °C (ether), $[\alpha]^{20}_D$ -60.5° (*c* 1.0, methanol). Also the benzamide derivative gave white needles; mp 134 °C (ether, petroleum ether), $[\alpha]^{22}_D$ -7.0° (*c* 0.5, methanol); lit.[17] mp 134 °C (ethyl acetate, petroleum ether), $[\alpha]_D$ -7.3° (methanol).
(22) Methyl *N*-acetyl-3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside; mp 161-162 °C, $[\alpha]^{22}_D$ -22.3° (*c* 1.0, methanol); lit. mp 163-164 °C, $[\alpha]^{22}_D$ -24.0° (*c* 1.0, methanol). See: Kuhn, R.; Kirschenlohr, W. *Chem. Ber.* **1953**, *86*, 1331-1333.

Binuclear Platinum(II) Photochemistry. Rates of Hydrogen Atom Transfer from Organometallic Hydrides to Electronically Excited $Pt_2(P_2O_5H_2)_4^{4-}$

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Previous investigations have established that the triplet $d\sigma^*p\sigma$ excited states of d^8-d^8 binuclear complexes ($^3M_2^*$, M = Rh, Ir, Pt) are readily oxidized by one-electron acceptors.[2-5] A related but largely unexplored reaction for these $^3M_2^*$ states is hydrogen atom abstraction, $RH + {}^3M_2^* \rightarrow R^\bullet + {}^\bullet M_2H$, a step that was proposed by Roundhill[6] to be a primary process in the Pt_2-photocatalyzed conversion of isopropyl alcohol to acetone and dihydrogen ($Pt_2 = Pt_2(P_2O_5H_2)_4^{4-}$). Support for Roundhill's proposal has come from work in our laboratory[5] that has shown that $^3Pt_2^*$ will abstract hydrogen atoms from a large number of different substrates.

Because of the potential importance of H atom transfer in hydrocarbon and related small-molecule activation processes, we are engaged in studies involving systematic variations in the substrate donor to $^3Pt_2^*$: our aim is to elucidate the factors that control the reaction rates. Here we report the results of kinetic studies of H atom transfers from organometallic hydrides to $^3Pt_2^*$:

$$^3Pt_2^* + R_3EH \xrightarrow{k_H} {}^\bullet Pt_2H + R_3E^\bullet \qquad (1)$$

where E = Si, Ge, Sn and R = alkyl or phenyl. Observation of Pt_2H_2 as a reaction product[7] together with the measured kinetic isotope effect (vide infra) indicates that H atom transfer, (1), is the primary step involved in the photoreactivity of Pt_2 with R_3EH.

The rate constants (eq 1) were measured from the quenching of the $^3Pt_2^*$ emission (τ_0 = 10 μs) by R_3EH in degassed acetonitrile solution at 298 K, employing a Nd-YAG laser (excitation at 355 nm, 8-ns fwhm). Linear Stern-Volmer plots following the equation $\tau_0/\tau = 1 + k_H\tau_0[R_3EH]$ (τ and τ_0 are the excited-state lifetimes in the presence and absence of the hydride) were obtained.

Because the rate constants for diffusion of the reactants and for encounter-pair dissociation are not expected to vary appreciably in the R_3EH series, the k_H values should be a good measure of the reactivity of $^3Pt_2^*$. It is apparent from the data in Table I that the reactivity of $^3Pt_2^*$ toward R_3EH decreases in the order Sn > Ge >> Si. This trend qualitatively parallels that of hydrogen abstraction by *tert*-butoxy radicals, although the latter is much less pronounced (Table I). The observed rate constants decrease as the E-H bond energy increases (Sn < Ge < Si).[8] The general tendency of R_3EH species to undergo radical reactions decreases in the same order as k_H. For example, addition to olefins and reduction of organic halides usually take place by radical mechanisms for both Sn and Ge; however, for Si, a catalyzed polar mechanism is preferred.[9] The triphenyl derivatives react with

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