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, $CHCl_3$).

(16) All new compounds cited in this article gave satisfactory elemental analysis.

(17) Similar results were observed with the equivalent phenyloxazoline; see: Jacquinet, J. C.; Sinay, P. *Carbohydr. Res.* **1974**, *32*, 101–114.

(18) Methyl 2-amino-2-deoxy-α-D-arabinofuranoside (**4**); mp 78–81 °C (ethyl acetate); lit.[19] 75–77 °C (ethyl acetate), $[\alpha]^{22}_D$ +135° (*c* 0.4, methanol); lit.[20] $[\alpha]_D$ +128° (*c* 1.0, methanol).

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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 dσ*pσ 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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(7) The dihydride was identified by its absorption spectrum ($\sigma \rightarrow d\sigma^*$ at 314 nm)[5] and by ^{31}P NMR (δ 27.9, J(P,H) = 7.3 Hz, ^1J(P,Pt) ≅ 2180 Hz). For E = Sn or Ge, another reaction product, $Pt_2(R_3E)_2$, is formed (Vlček, A., Jr.; Gray, H. B., manuscript in preparation).

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Table I. Rate Constants (k_H)[a] for Hydrogen Atom Transfer Reactions

H atom donor	$^3Pt_2^*$	t-BuO$^\bullet$	t-Bu$^\bullet$
Et_3SiH	2.0×10^4	5.7×10^6 [b]	
Ph_3SiH	1.6×10^5	1.1×10^7 [b]	
Ph_3GeH	2.9×10^7	8.9×10^7 [b]	
Ph_3SnH	1.0×10^8	4.0×10^8 [b]	3.1×10^6 [d]
Bu_3SnH	1.2×10^7	2.2×10^8 [c]	7.4×10^5 [d]
Bu_3SnD	6.9×10^6	1.8×10^8 [c]	2.7×10^5 [d]

[a] Rate constants in $M^{-1}\ s^{-1}$. Values for $^3Pt_2^*$ measured in acetonitrile at 298 K, t-BuO$^\bullet$ reactions studied in 1:2 (v/v) benzene/t-Bu_2O_2. [b] Chatgilialoglu, C.; Ingold, K. U.; Lusztyk, I.; Nazran, A. S.; Scaiano, J. C. *Organometallics* **1983**, *2*, 1332–1335. T = 300 K. [c] Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 5399–5400. T = 295 K. [d] Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 7047–7055. T = 298 K in benzene.

Table II. Hydrogen Atom Transfer from Bu_3SnH to Electronically Excited Acceptors

acceptor	excited state	E_T[a]	k_H[c]
acetone	$n\pi^*$	78	2×10^8 [d,g]
benzophenone	$n\pi^*$	69	4.7×10^7 [e,g]
2-acetylnaphthalene	$\pi\pi^*$	58	2.0×10^6 [e,g]
Pt_2	$d\sigma^*p\sigma$	57.7[b]	1.2×10^7 [f]
1-naphthaldehyde	$\pi\pi^*$	56.4	1.1×10^6 [e,g]
biacetyl	$n\pi^*$	55	1.5×10^7 [e,g]

[a] Triplet energies in kcal mol^{-1}; data from ref 13, p 290, and from: Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; pp 3–21. [b] Heuer, W. B.; Totten, M. D.; Rodman, G. S.; Hebert, E. J.; Tracy, H. J.; Nagle, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 1163–1164. [c] Rate constants in $M^{-1}\ s^{-1}$ measured at room temperature. [d] In n-hexane. [e] In benzene. [f] In acetonitrile. [g] Reference 14, p 93.

$^3Pt_2^*$ faster than the trialkyls, which is analogous to rates found with both *tert*-butoxy and *tert*-butyl radicals (Table I).

The kinetic isotope effect measured for the reaction of $^3Pt_2^*$ with Bu_3SnH, $k_2(H)/k_2(D) = 1.7$, is in accord[10] with H atom transfer involving a linear Pt–H–Sn transition state with negligible charge transfer.[12-14] This value lies between those found for the reaction of Bu_3SnH with alkyl[15] (2.3 for Me$^\bullet$ and n-Bu$^\bullet$, 1.9 for Et$^\bullet$) and t-BuO$^\bullet$ radicals (1.2, Table I). Relative to the zero-point energy value,[10] the isotope effect is only slightly lower for the H atom transfer to $^3Pt_2^*$ from Bu_3SnH than from the α-(C–H) bond in $PhCH(OH)CH_3$ (4.7).[16]

Interestingly, the rate constants for H atom transfer are at least 2 orders of magnitude lower than those for electron transfer[3,17] at comparable driving forces.[18] A severe orientation requirement related to the formation of a linear Pt–H–E transition state is the likely explanation of this difference.

Rate constants for H atom transfer from Bu_3SnH to different excited triplet acceptors are set out in Table II. It is interesting that the reactivity of $^3Pt_2^*$ toward Bu_3SnH is comparable to that of the $n\pi^*$ excited states of ketones with similar triplet energies, being greater than that of $\pi\pi^*$ excited states of organic carbonyls. All d^8–d^8 complexes possess two open axial coordination sites. Excitation of Pt_2 strongly activates these sites, producing a highly energetic (E_T = 57.7 kcal mol^{-1}) species with an unpaired electron in an axially localized $d\sigma$-antibonding orbital. It would appear that this localized $d\sigma^*$ electron plays the same role in the reactivity of $^3Pt_2^*$ as a nonbonding, oxo-localized electron does in the chemistry[13,14] of excited organic carbonyls.

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Total Synthesis and Absolute Configuration of 7,20-Diisocyanoadociane

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7,20-Diisocyanoadociane (**1** or mirror image), a marine natural product from *Adocia* sp.,[1] is noteworthy in terms of structure, unprecedented biosynthesis,[1,2] and key position in a growing class of diterpenoid isocyanides.[3] The synthesis of **1** has been a conspicuous problem which has been taken as a challenge by a number of research groups. Reported herein is the first synthesis of this interesting perhydropyrene by an enantioselective route which permits assignment of the absolute configuration indicated in **1**.[4]

The acid chloride **2**, readily available in two steps from (1*R*, 2*S*, 5*R*)-(−)-menthol and glutaric anhydride (heating at 90 °C for 10 h followed by reaction with oxalyl chloride in benzene at 23 °C, 75% overall), was converted into vinyl ketone **3** (1.1 equiv of vinyltri-n-butylstannane in tetrahydrofuran (THF) with 0.34 mol % of $Pd(PPh_3)_4$ at 70 °C for 2 h, 90% yield).[5,6] Enone **3** was transformed into the corresponding ethylene ketal (90% overall yield) by a new method consisting of two steps: (1) treatment of a 1 M solution of **3** in $CHCl_2$ with (phenylseleno)trimethylsilane[7] (1.3 equiv), ethylene glycol (5 equiv), and I_2 (0.025 equiv) at 65 °C for 4 h to form the β-(phenylseleno) ethylene ketal (99%); (2) oxidation of selenide to selenoxide (1.5 equiv of m-chloroperbenzoic acid in CH_2Cl_2 at −20 °C for 15 min) followed by addition of dimethyl sulfide (0.8 equiv) and diisopropylamine (3 equiv) and warming to 60 °C to effect elimination (6.5 h at 60 °C), and finally gradient elution chromatography on silica gel (sg)(hexane–ether). Attempts to prepare this ketal by conventional acid-catalyzed direct ketalization were not successful.

The conversion of the ethylene ketal of **3** to diester **4** depended on new methodology for enantioselective and diastereoselective Michael addition which has recently been reported.[8] The ester enolate of the ketal **3** was generated at −78 °C in THF using 1.1 equiv of lithium diisopropylamide (LDA) for 45 min, methyl crotonate (1.1 equiv, E isomer) was added, the reaction mixture was quenched (HOAc) after 1 h at −78 °C, and the product was isolated by extractive workup and sg flash chromatography. The major Michael adduct (80% yield) was, as expected, the desired threo isomer **4** (threo/erythro ratio 8:1, ca. 60% ee).[8,9] Removal

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