evidence for ligand hydrogenation. On the other hand, styrene is extremely rapidly hydrogenated in the DMT/$PhSiH_3$ system.[22]

We are pursuing the synthesis of analogues of **2** with alkyl-substituted indenyl ligands, in an attempt to circumvent the disorder problem and get more precise structural parameters for this type of molecule. We are also undertaking a more general development of the chemistry of Cp(arene)TiX complexes.

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Registry No. 1, 49596-02-3; **2a**, 136910-76-4; **2a**-d_2, 136910-77-5; **2b**, 137036-29-4; **2b**-d_2, 137036-30-7; indane, 496-11-7; styrene, 100-42-5; phenylsilane, 694-53-1; deuteriosilane, 13587-51-4.

Supplementary Material Available: A complete crystal structure report for **2** including experimental details, positional and thermal parameters, bond distances and angles, least-squares planes, and atomic coordinates (27 pages); listing of observed and calculated structure factors for **2** (20 pages). Ordering information is given on any current masthead page.

Oxidative Addition of Palladium(0) to the Anomeric Center of Carbohydrate Electrophiles

Garth S. Jones and William J. Scott*

Department of Chemistry, The University of Iowa
Iowa City, Iowa 52242

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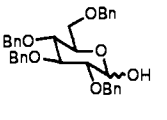
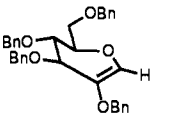
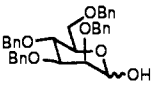
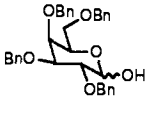
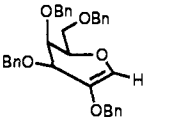
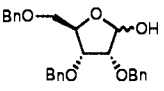
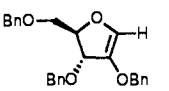
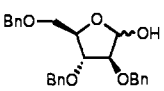
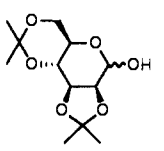
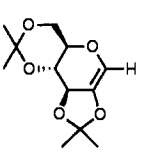
Palladium-mediated processes have been applied to the synthesis of biologically active carbohydrates in a variety of ways.[1-3] Daves[1] and others[2] have explored the use of Heck-type reactions using 1,2-anhydro sugars (glycals) as the olefin moiety. Glycals have also been metalated at the anomeric center and then coupled with aryl electrophiles using palladium(0) catalysts under classic cross-coupling conditions.[4,5] Earlier studies by this group[6] and others[7] led to the hypothesis that unactivated α-alkoxy electrophiles should be sufficiently reactive to allow oxidative addition to occur. Herein we wish to report the first use of a palladium-catalyzed process involving oxidative addition into the anomeric center of a carbohydrate derivative.

Table I. Two-Step Oxyglycal Synthesis

entry	carbohydrate	glycal	^{1}H NMR δ H-1	isolated yield (%)
1	 **1**	 **2**	6.31	87
2	 **3**	**2**		53
3	 **4**	 **5**	6.17	21[a]
4	 **6**	 **7**	6.17	60
5	 **8**	**7**		58
6	 **9**	 **10**	6.22	15

[a] dppfPd(0) (10 mol % dppfPdCl_2, 12 mol % *n*-BuLi) was used in place of Pd(PPh_3)$_4$.

Sulfonate esters have been employed as electrophiles in Heck olefinations and cross-coupling reactions.[6d,8] Treatment of tetra-*O*-benzylglucopyranose with freshly prepared[9] methanesulfonic anhydride in the presence of *s*-collidine yielded the corresponding mesylate.[10] Subsequent treatment with 0.9-5 mol % Pd(PPh_3)$_4$ at 50 °C resulted in oxidative addition followed by β-hydride elimination to afford tetra-*O*-benzylglucal **2** in high yield (Table I).[11] Oxyglycal **2** is readily identified by the vinyl hydrogen resonance at 6.31 ppm in the ^{1}H NMR spectrum.[12,13] In the absence of palladium, no glycal formation was observed.

To probe the generality of this reaction, a variety of protected sugars were subjected to the reaction conditions. Tetrabenzylmannose **3** underwent the two-step dehydration to give oxyglycal

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(7) For oxidative addition into (a) activated thioacetals, see (1) Yang, P.-F.; Ni, Z.-J.; Luh, T.-Y. *J. Org. Chem.* **1989**, *54*, 2261-2262; (2) Ni, Z.-J.; Yang, P.-F.; Ng, D. K. P.; Tzeng, Y.-L.; Luh, T.-Y. *J. Am. Chem. Soc.* **1990**, *112*, 9356-9364; (3) Shi, X.; Luh, T.-Y. *Organometallics* **1990**, *9*, 3019-3020; (b) acetals, see (1) Mukaiyama, T.; Soga, T.; Takenoshita, H. *Chem. Lett.* **1989**, 997-1000; (2) Mukaiyama, T.; Takenoshita, H.; Yamada, M.; Soga, T. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3122-3131.

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(10) Leroux, J.; Perlin, A. S. *Carbohydr. Res.* **1967**, *67*, 163-178.

(11) General procedure: A solution of tetra-*O*-benzylglucose (1.08 g, 2.0 mmol) in CH_2Cl_2 (20 mL) was treated with Ms_2O (0.70 g, 4.0 mmol) and collidine (0.80 mL, 6.0 mmol) and allowed to stir at room temperature for 1 h. To the clear, dark brown solution was added Pd(PPh_3)$_4$ (23 mg, 1 mol %), and the mixture was heated under argon at 50 °C overnight. The solution was then diluted with CH_2Cl_2 (20 mL), washed with 10% HCl (25 mL) and a saturated NaCl solution (25 mL), dried over $MgSO_4$, filtered through a plug of silica gel (1 × 2.5 cm), and purified by radial chromatography (SiO_2, 10% EtOAc in hexanes) to give 0.91 g of the oxyglucal (87%) as a white solid. (NOTE: Yields drop precipitously if the Ms_2O is even *slightly* decomposed; best results were obtained if the Ms_2O had been prepared[9] within 1 week of use.)

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0002-7863/92/1514-1491$03.00/0

2, albeit in lower yield. Reaction of the mesylate of tetrabenzylgalactose **4** gave the expected oxyglycal, **5**, in low (15%) yield. Reaction with dppfPd(0) (vide infra) resulted in a slightly better yield of oxyglycal **5** (Table I, entry 3).

Carbon–mesylate bonds possess significant ionic character, so it may be more proper to consider the sugar as consisting of an oxonium ion and a dissociated mesylate prior to oxidative addition.[14] Also, Daves has shown that if the palladium is sufficiently ligated, it is possible to suppress β-hydride elimination entirely and produce a stable palladium complex with a cis β-hydrogen.[15] Thus, the conformation of the oxonium ion and the stability of the palladium intermediate, not the stereochemistry at C-2, appear to be important factors in the effectiveness of this process (entries 1-3).

Treatment of ribose **6** and arabinose **8** under the reaction conditions at room temperature gave essentially the same amount of the corresponding oxyglycal (20%). A brief survey of bases (Ag_2CO_3, Na_2CO_3, NaH, and Proton Sponge) and metal catalysts ($(PPh_3)_2Pd(0)$, $Pd(AsPh_3)_4$, and dppfNi(0)) gave similar or lower yields. Using dppfPd(0), glycal **7** was obtained in 40% yield from ribose **6**, while arabinose **8** gave essentially no reaction. Heating to 50 °C with $Pd(PPh_3)_4$ as the catalyst resulted in dramatically improved yields for both sugars (Table I). Only a few examples of oxyglycals derived from furanoses have been reported.[16,17] Unlike the perbenzoyl analogue,[18] oxyribal **7** is thermally stable and may, therefore, prove to be synthetically useful.

The oxyglycal[20] obtained from 2,3:4,6-bis(isopropylidene)-mannopyranose **9**,[21] represents a new class of acetal-protected oxyglycals, which is unavailable by classic methods. Formation of oxyglycal **10** provides an indication of the gentleness of the oxidative addition, β-hydride elimination process. The properties of oxyglycal **10** have not been fully investigated, but it is stable to brief contact with aqueous acid and silica gel. Attempts to optimize the reaction conditions for acetal-protected carbohydrates are currently underway.

In summary, this work demonstrates the first example of palladium(0) oxidative addition into the anomeric center of carbohydrate electrophiles. Subsequent β-hydride elimination affords a new route to oxyglycals, including examples which cannot currently be prepared by other means. Further studies on the application of these novel electrophiles in other palladium-mediated reactions and on the use of oxyglycals in C-nucleoside synthesis are currently underway.

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Supplementary Material Available: TLC, IR, LCMS, and ^1H and ^{13}C NMR spectral data for compounds **2** and **7** as well as ^1H and ^{13}C NMR spectral data for compound **10** (2 pages). Ordering information is given on any current masthead page.

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Dyotropic (6 + 4)-Hydrogen Migration in a 2,3-Bis(methylene)decahydroanthracene

Heinz Geich, Wolfram Grimme,* and Kathrin Proske

Institut für Organische Chemie der Universität Köln Greinstrasse 4, D-5000 Köln 41, Germany

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The $4n$-electron homology is firmly established for pericyclic reactions by theory as well as by experiment. However, in one instance, the dyotropic hydrogen migration,[1] the number of reorganizing electrons is still limited to $4\sigma + 2\pi$. We now report on the dyotropic hydrogen migration in 2,3-bis(methylene)-1,2,3,4,4a,5,8,9,9a,10-decahydroanthracene-4a,9a-dicarboxylic anhydride **4**, which involves $4\sigma + 6\pi$ electrons.

The synthesis of the starting material **4** is illustrated in Scheme I: Cycloaddition of 1,2-bis(methylene)cyclobutane[2] to acetylenedicarboxylic acid, accompanied by dehydration, gives anhydride **1**.[3] Diels–Alder addition of **1** to 1,2-bis(methylene)-cyclohex-4-ene (**2**)[4] yields compound **3**,[3] which can be converted to **4**[3] by heating to 117 °C. Thermolysis of **4** at 150 °C yields 2,3-dimethyl-*cis*-1,4,4a,9,9a,10-hexahydroanthracene-4a,9a-dicarboxylic anhydride **5**[3] via dyotropic migration of the anti hydrogens at positions 5 and 8.

The kinetic parameters of this process were determined by monitoring the UV spectra of degassed, sealed samples of **4** in isooctane ($0.9\ 10^{-3}$ M) at six temperatures from 160 to 185 °C. The first-order rate constant k changes with temperature according to the Arrhenius equation

$$\log k = (11.1 \pm 1.1) - (31500 \pm 2100)/2.3RT \qquad (R = 1.98\ \text{cal/K·mol}) \quad (1)$$

The transition state for the conversion **4** → **5** requires a folded conformation in which the migrating hydrogens are near the termini of the diene. Force field calculations[5] show that **4f** (Scheme II) possesses a 2.9 kcal/mol higher enthalpy of formation than the preferred open form **4o**. When this preequilibrium is considered, the activation energy for the (6 + 4)-dyotropic hydrogen migration is 28.6 kcal/mol, close to the values reported (25.1–28.2 kcal/mol) for the (4 + 2)-dyotropic shift in conformationally rigid isodrin systems.[6]

In order to investigate the mechanism of this reaction, tetra- and dideuterated **4** were prepared from appropriately labeled **2**: **2**-d_4 was obtained by cycloaddition of 1,1,4,4-tetradeuteriobutadiene[7] to dimethyl acetylenedicarboxylate and transformation of the ester groups into methylene groups via reduction to the diol ($LiAlH_4$), formation of the dibromide (PBr_3), and debromination (Zn-Cu).

The electrochemical reduction of benzocyclobutene in THF–D_2O[8] yielded a 1:1 mixture of *cis*- and *trans*-2,5-dideuterio-

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(3) Spectral data and physical constants for new compounds are as follows (^1H NMR spectra at 300 MHz, ^{13}C NMR spectra at 75.5 MHz in $CDCl_3$). **1**: mp 178 °C; ^1H NMR δ 2.60 (s, 4 H), 3.05 (s, 4 H). Anal. Calcd for $C_{10}H_8O_3$: C, 68.18; H, 4.58; O, 27.24. Found: C, 67.82; H, 4.88; O, 27.30. **3**: mp 175 °C dec.; ^1H NMR δ 5.66 (s, 2 H), 2.50 (m, 14 H), 2.05 (t, J = 1.6, 2 H); ^{13}C NMR δ 175.0, 137.4, 123.8, 122.4, 47.0, 38.9, 36.6, 30.8. Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43; O, 17.00. Found: C, 76.62; H, 6.62; O, 16.76. **4**: mp 175 °C dec.; ^1H NMR δ 5.42 (s, 2 H), 5.16 (s, 2 H), 4.65 (s, 2 H). 2.45 (m, 4 H), 2.13 (AB, $\Delta\nu$ = 126.2, J = 14.3, 4 H), 1.79 (AB, $\Delta\nu$ = 166.0, J = 14.4, 4 H); ^{13}C NMR δ 176.2, 139.0, 128.0, 124.3, 111.6, 51.0, 38.9, 36.6, 30.8; UV λ_{max} 245 nm (ϵ 7000), 280 (700). **5**: mp 177 °C; ^1H NMR δ 6.90 (AA'BB', 4 H), 2.50 (AB, $\Delta\nu$ = 167.3, J = 14.4, 4 H), 1.95 (AB, $\Delta\nu$ = 181, J = 14.6, 4 H), 1.38 (s, 6 H); ^{13}C NMR δ 176.6, 135.0, 128.3, 127.6, 53.0, 39.2, 37.1, 18.7; UV λ_{max} 248 nm (ϵ 1000).
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(6) Mackenzie, K.; Proctor, G. J.; Woodnutt, D. J. *Tetrahedron* **1987**, *43*, 5981.
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