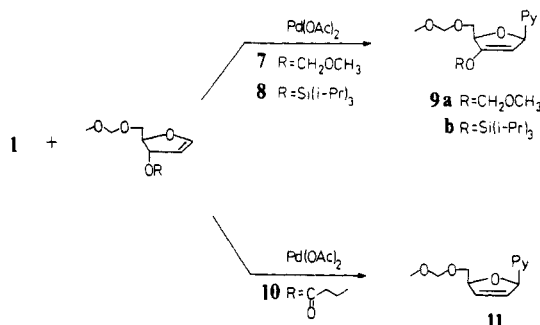
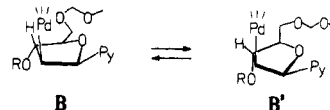


However, if the 3-hydroxyl substituent of this glycal was converted to an ester<sup>21</sup> (10), the directing effect on adduct formation<sup>1</sup> was retained while the improved leaving group changed the relative energetics for adduct decomposition modes. The observed product, formed by anti loss of palladium carboxylate, was (2'R)-cis-5-[2',5'-dihydro-5'-(methoxymethoxy)methyl]-2'-furanyl]-1,3-dimethyl-2,4-(1H,3H)pyrimidinedione<sup>17</sup> (11) which is a direct precursor to various important ribofuranosyl C-nucleosides.<sup>22,23</sup>



In the five-membered ring series, unlike the six, it is typical that multiple, essentially isoenergetic conformations coexist in solution.<sup>24</sup> The nature, number, and position of substituents on the furanosyl ring affect conformational preferences significantly,<sup>25</sup> making difficult the prediction

of favored conformation(s) for specific molecules. In conformation B, which has the large groups at C<sub>1</sub> and C<sub>4</sub> in favorable pseudoequatorial positions, palladium and  $\beta$ -hydrogen are essentially syn-periplanar<sup>26</sup> as required for syn  $\beta$ -hydride elimination (which is facile in furanoid systems).<sup>1,5</sup> However, the favorable leaving ability of carboxylate diverts the reaction to anti palladium carboxylate elimination, presumably following a suitable conformational change to B'.



The combination of regio- and stereocontrol of adduct formation previously achieved and stereoelectronic control of adduct decomposition provides an effective and versatile synthetic approach to C-nucleosides. Continued experimental and theoretical<sup>27</sup> study of mechanistic details of organometallic reactions foreshadows the development of synthetic procedures of increasingly impressive specificity.

**Acknowledgment.** We thank the American Cancer Society for financial support. We thank H. Henrik Johnsson for preparation of starting materials for pyranoid glycals.

(21) Ireland, R. E.; Anderson, R. C.; Badoud, R.; Fitzsimmons, B. J.; McGarvey, G. J.; Thaisrivongs, S.; Wilcox, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 1988–2006.

(22) Hacksell, U.; Daves, G. D., Jr. *J. Org. Chem.* **1983**, *48*, 4144–4147.

(23) Hirota, K.; Watanabe, K. A.; Fox, J. J. *J. Org. Chem.* **1978**, *43*, 1193–1197.

(24) Lesyng, B.; Saenger, W. *Carbohydr. Res.* **1984**, *133*, 187–197.

(25) Wioriewicz-Kuczera, J.; Rabczenko, A. *J. Chem. Soc., Perkin Trans. 2* **1985**, 789–797.

(26) The agostic interaction between these substituents<sup>27a</sup> helps stabilize the conformation.

(27) (a) Koga, N.; Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1985**, *107*, 7109–7116. (b) Backvall, J. E.; Bjorkman, E. E.; Pettersson, L.; Siegbahn, P. *J. Am. Chem. Soc.* **1985**, *107*, 7265–7267. (c) Brainard, R. L.; Whitesides, G. M. *Organometallics* **1985**, *4*, 1550–1557. (d) Bryndza, H. E. *J. Chem. Soc., Chem. Commun.* **1985**, 1696–1698.

## Additions and Corrections

Robert W. Armbruster, Michael M. Morgan, James L. Schmidt, Chun Man Lau, Rose M. Riley, Daniel L. Zambrowski, and Harold A. Dieck\*: Palladium-Catalyzed Additions of Amines to Conjugated Dienes: Alteration of Behavior of (Triphenylphosphine)palladium Catalysts with Amine Hydroiodide Salts. **1986**, *5*, 234–237.

On page 236, left column, line 51, the word “not” should be deleted. Thus the sentence beginning on line 49 should read: “After 9 h, greater than 85% conversion (GLC) to the 1,4-addition product *N*-(1-buten-1-yl)-*p*-toluidine had occurred.”

T. K. Dutta, J. C. Vites, and T. P. Fehlner\*: On the Mechanism of the Hydrogenation/Dehydrogenation of a C<sub>2</sub> Fragment on a Triiron Site. **1986**, *5*, 385–386.

In the caption to Figure 1 the calculated mass for HD<sub>2</sub>Fe<sub>3</sub>(CO)<sub>9</sub>CCH<sub>3</sub> should read 451.8186.