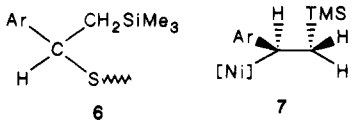
action may proceed via the first coupling reaction with 4 to give the intermediate 6 which may undergo an oxidative addition[15] with a Ni(0) species to afford 7.[8] A β-elimi-



6 7

nation process may then occur to yield the corresponding vinylsilane. The requirement of cis coplanarity of Ni–C–C–H atoms for β-elimination and the steric effect of the silyl group determine the stereochemistry of product.[16]

In summary, we have depicted a convenient synthesis of vinylsilanes from dithioacetals. Thus, our method provides a short passage for the stereoselective transformation of aldehyde to vinylsilane via dithioacetal which is readily accessible.

Acknowledgment. We thank the Croucher Foundation for generous support. Z.J.N. thanks Beijing-Hong Kong Academic Exchange Centre for support and the Lee Hysan Foundation for a fellowship.

Registry No. **3a**, 5616-55-7; **3b**, 67810-92-8; **3c**, 113509-20-9; **3d**, 6712-20-5; **3e**, 5769-01-7; **3f**, 69922-37-8; **3g**, 113509-21-0; **3h**, 23229-32-5; **3i**, 113509-22-1; **3j**, 6317-10-8; **4**, 13170-43-9; **5a**, 19372-00-0; **5b**, 113509-23-2; **5c**, 113509-24-3; **5d**, 76711-42-7; **5e**, 113509-25-4; **5f**, 113509-26-5; **5g**, 113509-27-6; **5h**, 113509-28-7; **5i**, 113509-29-8; **5j**, 51318-07-1; $NiCl_2(PPh_3)_2$, 14264-16-5.

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(17) Lee Hysan Foundation Graduate Fellow, 1986–87.

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Electrophilic Amination as a Route to Deoxyamino Sugars: Synthesis of the Key Intermediate for 1β-Methylcarbapenem

Summary: The application of electrophilic amination of keto sugars as a route to deoxyamino sugars by the reaction of sugar enolates with dibenzyl azodicarboxylate has been explored. Although the success of the reaction is dependent on several factors, such as the location of the carbonyl group and the substitution pattern on the pyranosidulose ring, the process is synthetically promising. This has been demonstrated by preparation of the protected Melillo Lactone analogue **18**, a key intermediate for 1β-methylcarbapenem.

Sir: In most procedures for the preparation of deoxyamino sugars, the nitrogen is introduced as a nucleophile which displaces a leaving group[1] or reacts with an electrophilic site[2,3] in a pyranoside partner. Electrophilic amination[4,5]

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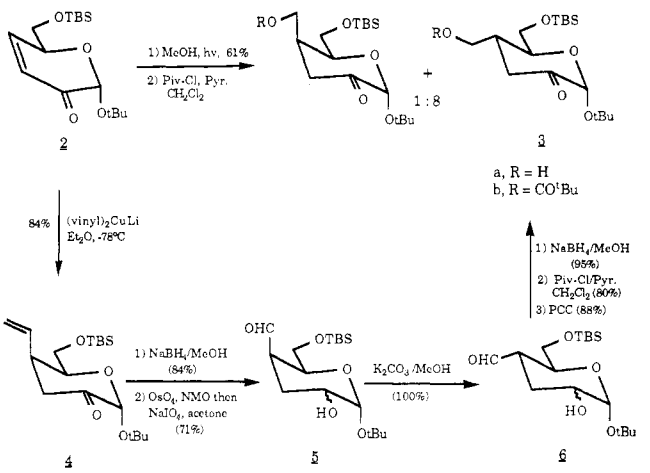
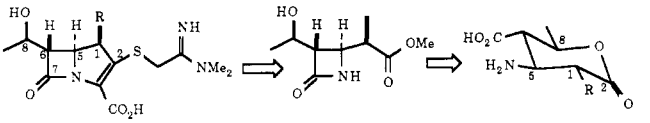
Scheme I



has been unexplored, in spite of the availability of a wide variety of ketonic sugars which conceivably could be suitable nucleophilic partners. In this manuscript, we report some of our work on electrophilic amination of sugars in the context of a formal total synthesis of 1β-methylcarbapenem (**1a**).[6,7]



Our interest in this project grew out of an unexpected observation in connection with our continuing interest in the mechanistic details of photochemically induced addition of methanol to α-enones.[8–10] In all the substrates we have examined the photoaddition and normal conjugate additions proceeded with the same stereoselectivity.[8] However, with enone **2**,[11] photoaddition gave primarily the equatorial adduct **3a** (Scheme I), while normal conjugate addition displayed the opposite stereoselectivity. This was confirmed by degradation of adduct **4** to the aldehyde **5** and epimerization to give **6**. The latter was then converted into the photoadduct, **3a**, by standard operations (Scheme I).

(2) (a) Horton, D.; Weckerle, W. *Carbohydr. Res.* **1975**, *44*, 227. (b) Pelyvás, I.; Sztaricskai, F.; Bognár, R. *Carbohydr. Res.* **1979**, *76*, 257. (c) Pelyvás, I.; Hasegawa, A.; Whistler, R. L. *Carbohydr. Res.* **1986**, *146*, 193.

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(11) Enone **2** was prepared via a Ferrier reaction of 2-acetoxytriacetylglucal with *tert*-butyl alcohol, followed by base hydrolysis of the product. [Ferrier, R. J.; Prasad, N. *J. Chem. Soc., C* **1969**, 570.] We are greatly indebted to Professor Ferrier for a generous gift of the precursor to **2**.

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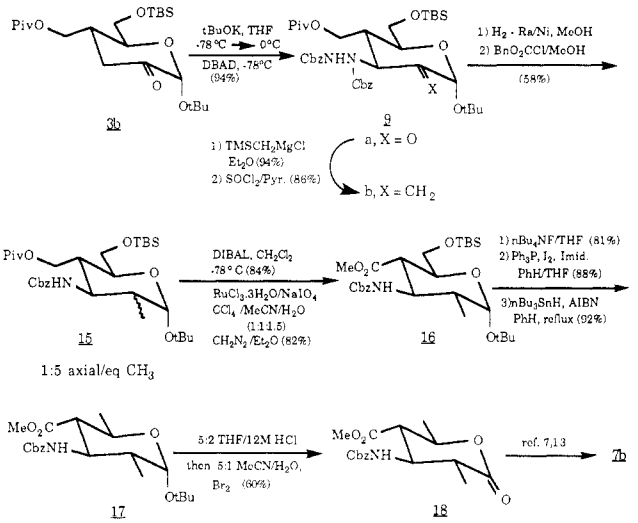
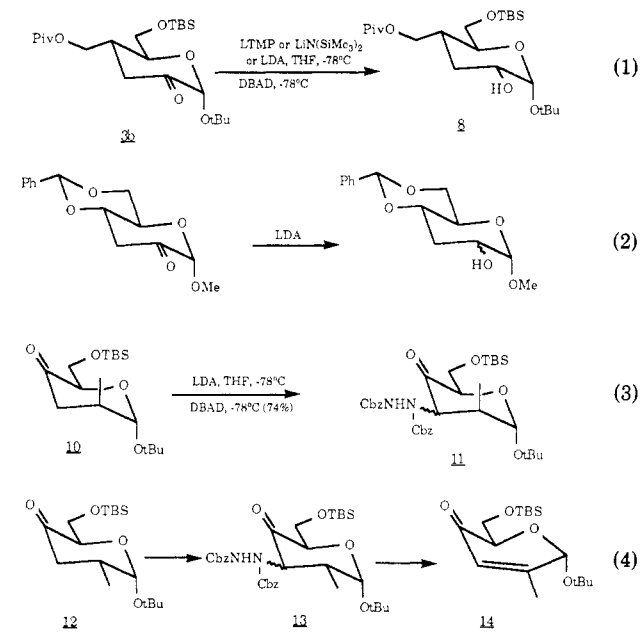
Scheme II



Although we are currently unable to offer a rationalization for these differences in stereoselection to give **3** and **4**, it was evident that the former was an attractive synthon for the synthetic carbapenem antibiotics.[6,7,12] The specific advantages for 1β-methylcarbapenem[6,7] can be appreciated by comparing the "Melillo lactone"[13] analogue **7b** with **3**. Thus, the hydroxymethyl and carbonyl groups of **3** are excellent implements for the carboxylic acid and C1 methyl groups of **7b**, respectively. The execution of an electrophilic amination would complete the retrosynthetic requirements for obtaining **7b** from **3a**, and a timely report by Trimble and Vederas[4a,16] suggested a solution.



However, treatment of ketone **3b** with LDA or lithium hexamethyldisilazide, followed by dibenzyl azodicarboxylate (DBAD),[16] led to the alcohol **8** (eq 1), instead of the aminated compound **9a** (Scheme II). A similar aberrant reduction of a pyranosid-2-ulose by LDA (eq 2) has been reported recently by Bonnert and Jenkins.[14] In contrast to these results, it was interesting to note that with the 4-ulose **10**, similar reaction conditions led to high yields of the amination product **11** (eq 3). With the epimeric methyl derivative **12**, amination did occur; but under the reaction conditions, the adduct **13** underwent ready elimination so that the degradation product **14** (eq 4) was formed in substantial amounts.

It transpires that deprotonation of **3b** could be achieved without incident by use of *t*-BuOK in THF, and subsequent addition of DBAD then led to the desired amination product **9a** in virtually quantitative yield. The most efficient procedure for obtaining the corresponding methylene derivative **9b** proved to be the addition of $TMSCH_2MgCl$[15] followed by reaction with thionyl chloride in pyridine. Hydrogenation in the presence of Raney nickel then gave the equatorial C2-CH_3 derivative (plus 15% of the C2 epimer) and simultaneously cleaved the hydrazine. Protection of the amine in situ led to compound **15** (Scheme II). The product was then ready for oxidation of one of the protected hydroxymethyl residues and deoxygenation of the other. These transformations were effected by standard procedures to obtain **16** and thence **17**. Hydrolysis of the glycoside and oxidation then afforded the protected Melillo lactone[13] analogue **18**, which is an established intermediate for a 1β-methylcarbapenem.[7]

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(16) We are grateful to Professor Vederas for disclosing details of his procedure prior to publication.

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Samarium Diiodide Promoted Intramolecular Pinacolic Coupling Reactions[1]

Summary: Samarium diiodide promotes intramolecular reductive coupling of functionalized keto aldehyde substrates, generating stereodefined 2,3-dihydroxycyclopentanecarboxylate derivatives.

Sir: Samarium diiodide (SmI_2) is an exceedingly useful reagent for promoting intramolecular reductive coupling reactions. Investigations of such reactions have led to development of several useful and convenient strategies for construction of highly functionalized carbocycles and heterocycles. For example, intramolecular Barbier reactions,[3] intramolecular Reformatsky reactions,[4] intramo-

(1) Lanthanides in Organic Synthesis. 9.

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