methanol was mild and selective enough to leave the ester and *tert*-butoxycarbonyl groups unaffected.[20]

In conclusion, great versatility of the chiral synthons of type **2** should result from the smooth and stepwise displacements of substituents at the 4- and 5-positions of oxazolidinone heterocycles, as described here for a few examples.[21] Applications of the present methodology to the facile preparation of amino sugars and peptides of biological interest are now under investigation.

Supplementary Material Available: Experimental and spectral data for compounds **11b–13** and **11b–16** (3 pages). Ordering information is given on any current masthead page.

(20) Ishizuka, T.; Kunieda, T. *Tetrahedron Lett.* **1987**, *28*, 4185.
(21) Typical functions other than groups presented here as R^1 and R^2 include cyano, cyanoethyl, carboxyethyl, and vinyl groups at 5-position and allyl, aryl, and acetonyl groups at 4-position. Ishizuka, T.; Ishihara, H.; Oosaki, M.; Kunieda, T.; Higuchi, T.; Hirobe, M. *The 18th Congress of Heterocyclic Chemistry*; Fukuoka: Japan, 1986; Abstract p 289.

Takehisa Kunieda,* Tadao Ishizuka
Faculty of Pharmaceutical Sciences
Kumamoto University
Oe-honmachi, Kumamoto 862, Japan

Tsunehiko Higuchi, Masaaki Hirobe*
Faculty of Pharmaceutical Sciences
University of Tokyo
Hongo, Tokyo 113, Japan
Received February 16, 1988

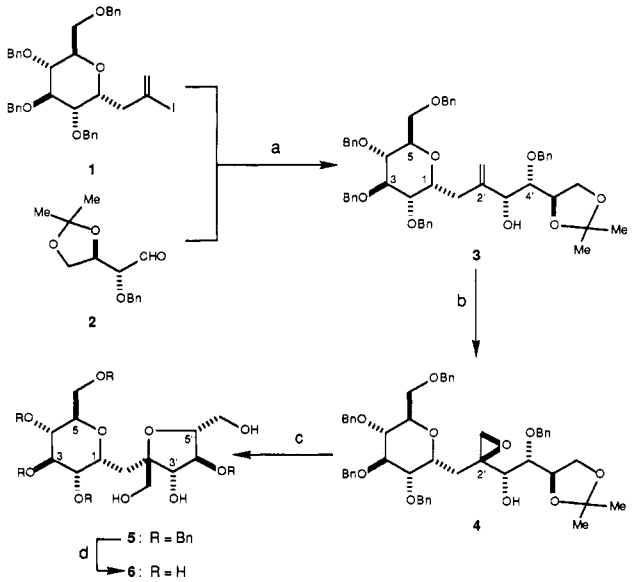
Synthesis of C-Sucrose

Summary: C-Sucrose has been synthesized in six steps from vinyl iodide **1** and aldehyde **2** with approximately 30% overall yield. The synthetic route developed is flexible enough to prepare C2′ and C3′ stereoisomers of C-sucrose and related compounds.

Sir: We have recently reported results of studies which examined the conformational preferences of certain C-disaccharides and showed that they could be favorably compared to their oxygen counterparts.[1] Our attention has now turned to other biologically important saccharides. One such project is to examine the conformational preference of C-sucrose and to study its effect on the sweetness receptor. The information gained from these studies would provide a valuable insight about the structure of the receptor, and could facilitate the rational design of nonnutritive sweeteners.[2] In this paper we wish to report the synthesis of C-sucrose.

The success of the synthesis depended on two key reactions (Scheme I). The first of these exploits the recently developed Ni(II)/Cr(II)-mediated coupling of vinyl iodides to aldehydes.[3] This reaction would provide a mild and convenient procedure for construction of the required carbon backbone from vinyl iodide **1** and aldehyde **2**. It was envisaged that the other key reaction, formation of the fructose ring of **5**, would involve acid-catalyzed ring-

Scheme I[a]



[a] Reagents and reaction conditions: (a) (1) $NiCl_2$ (0.1%)–$CrCl_2$/THF–DMSO (4:1)/room temperature; (2) $(EtO_2CN{=})_2$/P-$(Ph)_3$/$PhCO_2H$/PhH/room temperature; (3) K_2CO_3/MeOH/room temperature; (b) MCPBA/CH_2Cl_2/room temperature; (c) CSA/wet CH_2Cl_2 (saturated)/room temperature; (d) H_2 (1 atm)/10% $Pd(OH)_2$ on C/MeOH/room temperature.

opening of the epoxide **4** and concomitant cyclization by intramolecular attack of the secondary hydroxyl functionality.

The required fragments for the coupling reaction were readily available. Vinyl iodide **1** was synthesized from the corresponding vinyl bromide[4] in one step.[5] Aldehyde **2**[6] was synthesized from 2,3-*O*-dibenzyl-4,5-*O*-isopropylidene-D-arabinose[7] in three steps.[8] The unstable aldehyde **2** was used immediately in the coupling reaction with **1** to produce an approximately 10:1 mixture of the expected allylic alcohols.[9] The stereochemistry of the major product was tentatively assigned as erythro, based on previous examples of Ni(II)/Cr(II)-mediated couplings.[3a] Since the desired threo alcohol **3** was the minor product of the coupling, attempts were made to invert the stereochemistry at C3′. Among several possibilities examined a modified Mitsunobu procedure[10] gave the most satisfactory results.[11]

By utilizing the directing effect of the free allylic hydroxyl group, *m*-chloroperbenzoic acid (MCPBA) epoxidation[12] of the threo allylic alcohol **3** gave a 1:3 mixture of syn and anti epoxy alcohols in 94% yield. Conversely, the Ti(*i*-OPr)$_4$/*t*-BuO_2H epoxidation[13] yielded a 12:1 mixture of syn and anti epoxy alcohols in 72% yield. The

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(4) Hosami, A.; Sakata, Y.; Sakurai, H. *Tetrahedron Lett* **1984**, *25*, 2383.
(5) The vinyl bromide was treated with *t*-BuLi/THF/−78 °C, followed by iodine quench at −78 °C.
(6) For a synthesis of the antipode, see: Williams, D. R.; Klingler, F. D. *Tetrahedron Lett.* **1987**, *28*, 869.
(7) Babirad, S. A.; Wang, Y.; Kishi, Y. *J. Org. Chem.* **1987**, *52*, 1370.
(8) These three steps are: (a) MCPBA/CH_2Cl_2/phosphate buffer (pH 7)/room temperature. (b) $LiAlH_4$/Et_2O/0 °C. (c) Swern oxidation.
(9) The ratio was based on the isolated products.
(10) For a review on this subject, see: Mitsunobu, O. *Synthesis* **1981**, 1.
(11) Significant scrambling of the C3′ position occured when THF was employed as solvent, probably via the intermediacy of an allylic cation.
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(13) Isobe, M.; Kitamura, M.; Mio, S.; Goto, T. *Tetrahedron Lett* **1982**, *23*, 221 and references cited therein. MCPBA epoxidation of the triethylsilyl derivative of **3** yielded a 2:1 mixture of syn and anti epoxides.

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stereochemical assignment of epoxy alcohols was made on the basis of the literature precedent[12,13] and later confirmed by NOE experiments. Additional evidence for this assignment was secured by subjecting the threo allylic alcohol to Sharpless asymmetric epoxidation conditions [(+)- or (−)-diethyl tartrate (DET)/t-BuO_2H/CH_2Cl_2/O °C].[14] In the case of (+)-DET conditions we observed a ratio greater than 100:1 of syn and anti products, whereas (−)-DET showed a decrease in this ratio (60:40).[15,16]

Treatment of the threo anti epoxide **4** with camphorsulfonic acid (CSA) in wet CH_2Cl_2 gave the desired cyclized product **5** in 89% yield. Supporting evidence for the stereochemical assignments was obtained from NOE experiments on the triol 5, its C2′ and C3′ stereoisomers,[17] and their triacetoxy derivatives. In particular, irradiation of H5′ in **5** showed an enhancement of H3′ and H1′, and irradiation of H3′ enhanced H5′ and H1′.[18]

It is interesting to note two points about the cyclization process. First, each of the four isomeric epoxides,[17] when treated with CSA, generated a different isomer of **5**. This result establishes that no stereochemical scrambling occurs during the cyclization, and therefore the stereochemistry of the cyclization products was solely dictated by the stereochemistry of the epoxy alcohols. Second, acetonide cleavage generates two free hydroxyl groups, either a priori could open the epoxide by attack at the quaternary center. Exclusive attack by the secondary hydroxyl is due to a combination of factors, the most important being the ability of the secondary hydroxyl to adopt a more favorable trajectory than the primary hydroxyl.

Hydrogenolysis of the triol **5** afforded C-sucrose **6**, which gave satisfactory spectroscopic data (^1H and ^{13}C NMR, MS, IR, $[\alpha]_D$).[19] The overall yield of C-sucrose from the vinyl iodide **1** was approximately 30%. Using the same sequence of reactions, all the C2′ and C3′ stereoisomers of C-sucrose were also obtained from the corresponding stereoisomers of **4**.[20]

In summary, we have developed a concise and efficient synthesis of C-sucrose and its C2′ and C3′ stereoisomers, which may also have interesting biological activity. Studies are currently in progress to define the preferred conformation of C-sucrose[21] and to test its effect on the sweetness receptor.

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Supplementary Material Available: ^1H NMR spectra of key compounds and tables listing NOE data of the triol **5** and its C2′ and C3′ stereoisomers and their triacetates (15 pages). Ordering information is given on any current masthead page.

Ulrich C. Dyer, Yoshito Kishi*
Department of Chemistry
Harvard University
12 Oxford Street
Cambridge, Massachusetts 02138
Received April 8, 1988

Construction of β-Lactams by Highly Selective Intramolecular C–H Insertion from Rhodium(II) Carboxylate Catalyzed Reactions of Diazoacetamides

Summary: Intramolecular β-C–H insertion occurs in high yield and with exceptional selectivity in rhodium(II) carboxylate catalyzed decompositions of diazoacetamides.

Sir: A wide variety of methods have been developed for the construction of the β-lactam ring.[1] Among them, intramolecular carbenoid processes involving carbon–hydrogen insertion initially appeared to be attractive versatile procedures,[2] but despite extensive investigations,[3-6] both low yields and low selectivities in the photochemical and thermal decomposition of diazo amides limited further development of this methodology. Diazo ketones have subsequently been shown to undergo preferential intramolecular γ-C–H insertion in catalytic decompositions,[7-10] which offer advantages in product yields and selectivities over photochemical and thermal methods, and rhodium(II) acetate has been demonstrated to be the catalyst of choice for these transformations.[7] However, a limited number of examples of competitive β-C–H insertions have also been reported for catalytic decompositions of diazo carbonyl compounds,[6,11-13] although the cause for this unexpected

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(16) For a review of double diastereodifferentiation, see: Masamune, S.; Choy, W.; Peterson, J. S.; Sita, L. R. *Angew. Chem., Int. Ed. Engl.* 1985, *24*, 1.
(17) All the four C2′ and C3′ stereoisomers of **5** were obtained from MCPBA epoxidation of either erythro or threo allylic alcohols, followed by chromatographic separation, and then treatment with CSA in wet CH_2Cl_2.
(18) The tables listing NOE observed for the triol **5** and its C2′ and C3′ stereoisomers and their triacetates are included in the supplementary material.
(19) ^1H NMR (500 MHz, CD_3OD) δ 2.05 (2 H, m), 3.28 (1 H, t, J = 8.8 Hz), 3.52 (1 H, dd, J = 8.9 and 7.9 Hz), 3.46 (1 H, dd, J = 8.9 and 5.4 Hz), 3.63–3.85 (8 H, m), 4.08–4.13 (2 H, m), 4.25 (1 H, m); ^{13}C NMR (125 MHz, CD_3OD) δ 31.69, 62.79, 62.79, 65.15, 72.12, 72.80, 72.86, 74.58, 75.73, 77.55, 81.86, 84.18, 84.93; $[\alpha]_D$ +21.6° (c 0.3, MeOH).
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