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A simple and stereodivergent strategy for the synthesis of 3′-C-branched 2′,3′-dideoxynucleosides exploiting (*Z*)-but-2-en-1,4-diol and (*R*)-2,3-cyclohexylideneglyceraldehyde

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Abstract—Barbier type additions of allylic bromide **4**, derived from (*Z*)-but-2-en-1,4-diol **2** to (*R*)-2,3-cyclohexylideneglyceraldehyde **1** were performed through mediation with Zn employing Luche's procedure and also with low valent Cu, Co, and Fe which were produced via bimetal redox strategy in THF to afford **5c**,**d** as the major products. From these, **5a**,**b** were prepared following an oxidation–reduction protocol. Compound **5c** was exploited as a representative starting material to develop a simple and inexpensive strategy toward the synthesis of 3′-C-branched 2′,3′-dideoxynucleosides having stereodiversity at 3′- and 4′-positions.

From the time of the finding that a number of 2′,3′-dideoxynucleosides like ddI, ddC, AZT, etc. are effective therapeutic agents for the treatment of AIDS,[1a] the synthesis of nucleoside analogs has become a topic of ever increasing attention.[1] Various modifications of natural nucleosides of physiological and pharmaceutical interest were designed with the aim of attaining improved biological efficiency with minimal toxic effects. Incidentally, cellular kinases are more tolerant to modification in the sugar units than in the base moieties. Interest in the branched chain nucleosides[2] has been stimulated by their potential as antitumor and antiviral agents and a number of (2′- or 3′-)-C-branched-(2′- or 3′-)-deoxy and 2′,3′-dideoxy nucleoside analogs have been synthesized and evaluated in biological systems.[3] Moreover, in view of the current attention on antisense oligonucleotide therapeutics[4] of varied activities viz. antiviral, anticancer, antibacterial, etc., 3′-methylene branched nucleosides are used as building blocks for the preparation of the 3′-methylene-modified oligonucleotides with a view to attaining better enzymatic stability against exo/endo nucleases and also enhancing membrane permeability.[5] Hence, preparation of 3′-C-branched dideoxynucleoside analogs with varied stereochemical features drew attention.[6]

For the synthesis of a nucleoside analog, a convergent approach[1] involving the base coupling of a sugar unit with a nucleoside base using various established procedures,[7] has an inherent advantage since it provides an opportunity to carry out a desired chemical/stereochemical modification in the sugar unit prior to the coupling. Thus, designing and developing efficient syntheses of sugar units assumes considerable importance. The present work describes our endeavors to develop a very simple, efficient, and stereochemically flexible strategy for the synthesis of 3-C-branched sugars of the corresponding nucleosides through combined exploitation of easily accessible (*R*)-2,3-cyclohexylideneglyceraldehyde **1**[8a] and commercially available (*Z*)-but-2-en-1,4-diol **2**.

Monosilylation of **2** with TBDPS-chloride following a simple procedure used by us earlier[8b] afforded **3** in good yield (77%). The hydroxyl of **3** was brominated efficiently in two steps via mesylation and treatment of the mesylate with NaBr to produce allylic bromide **4** in a good yield. Zinc-mediated Barbier type addition of **4** to **1** was first performed following Luche's procedure[9] to obtain a mixture of all possible diasteromers (**5a**–**d**) of the homoallylic alcohol product, with 4,5-*anti*-3,4-*syn***5c**[10] and 4,5-*anti*-3,4-*anti***5d**[11] being the major products, separable by column chromatography. Compounds **5a** and **5b** were produced only in very small

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quantities and could not be separated from each other chromatographically (Table 1, entry 1). The same crotylation reaction was performed using three other metals (Co, Cu, Fe) as the promoters. The active metals were generated in situ according to bimetal redox strategy. The reactions were carried out by the addition of zinc powder to a stirred mixture of **1**, **4** and any one of the commercially available salts ($CoCl_2{\cdot}8H_2O$, $CuCl_2{\cdot}2H_2O$, and $FeCl_3$) in distilled THF and following an operationally simple procedure.[12] In each case, the overall reaction is likely to take place via reduction of the metal salt with zinc to produce the metal (Fe or Co or Cu) in any of their low valent states due to the fact that $E^0_{Zn=Zn^{2+}+2e}+0.761$ V; $E^0_{Co=Co^{2+}+2e}+0.280$ V; $E^0_{Fe=Fe^{2+}+2e}+0.441$ V and $E^0_{Fe^{2+}=Fe^{3+}+e}-0.771$ V; $E^0_{Cu=Cu^{2+}+2e}-0.337$ V. This was followed by the addition of **4** to **1** mediated by the low valent metal. The comparative results of all these metal mediated additions are shown in Table 1.

All the reactions yielded exclusively γ-addition products. For Cu and Co mediated additions (entries b and c), yields were comparable with that applying Luche's procedure (entry a); however, the reactions took place at a much slower rate. In contrast, Fe mediated addition (entry d) took place at a considerably faster rate and gave a better yield of the product. The good rate of the Fe-promoted reaction was presumably due to the high $\Delta E^0_{Fe(III)-Zn}$. However, the copper-mediated reaction was slow despite a high ΔE^0_{Cu-Zn}, as active copper tends to form larger sized beads on prolonged stirring which causes good loss of its reactivity. All the new metal-mediated reactions (entries b–d) were favored in ordinary THF (distilled only) due to appreciable solubility of the salts in the somewhat moist solvent.[13] In all cases, the freshly generated metals (Co, Cu, and Fe) remained active enough to promote the crotylation reaction even in such moist conditions. In all cases the metal/metal salts were taken in excess for total consumption of **1**. Moreover, the reactions were made faster by using Zn in powdered form ensuring the availability of more surface area. All these reactions (entries a–d) were associated with a similar pattern of stereoselectivities producing **5c** and **5d** as the major products and only a very small amount of the other two diastereomers (**5a** and **b**). Among them, Cu-mediated additions produced more **5d** in contrast with the other additions. There was a good improvement in the formation of **5c** for the Co-mediated reaction. Subsequently, the preparations of **5a** and **5b** were improved employing an oxidation–reduction strategy.[14] Thus PCC oxidation of **5c** or **5d** and reduction of the resulting ketones **6** or **7** with K-selectride[14a] furnished 2,3-*syn* products **5a**[15] or **5b**,[16] respectively, almost exclusively. As is evident from its mechanism,[14] the production of different reduction products **5a** or **5b** from the substrates **5c** or **5d** clearly establishes the 4,5-*anti* relationship originally present in the latter.

Thus, the preparation of substantial amounts of all the four possible diastereomers **5a–d** could be accomplished. To determine their relative 3,4-stereochemistry, one of them, **5d** was benzoylated and then deketalized by stirring its CH_2Cl_2 solution with aqueous CF_3COOH at 0 °C, to afford diol **9**. This was monosilylated at the primary hydroxyl and then ozonolyzed following a reported procedure[17] to produce γ-lactone **11**.[18] The ^{1}H NMR spectrum of **11** showed a doublet of doublets at 5.97 ($J = 13.7$, 2.4 Hz) indicating the *syn* ($J = 2.4$ Hz) and *anti* ($J = 13.7$ Hz) relationship of H-3 with its two neighboring protons H-2 and H-4, respectively, which in turn proves the *anti–anti* relationship of the corresponding H-4 in **5d**. Accordingly, the stereochemistry of all other diastereomers (**5a–c**) could be ascertained as shown in Scheme 1.

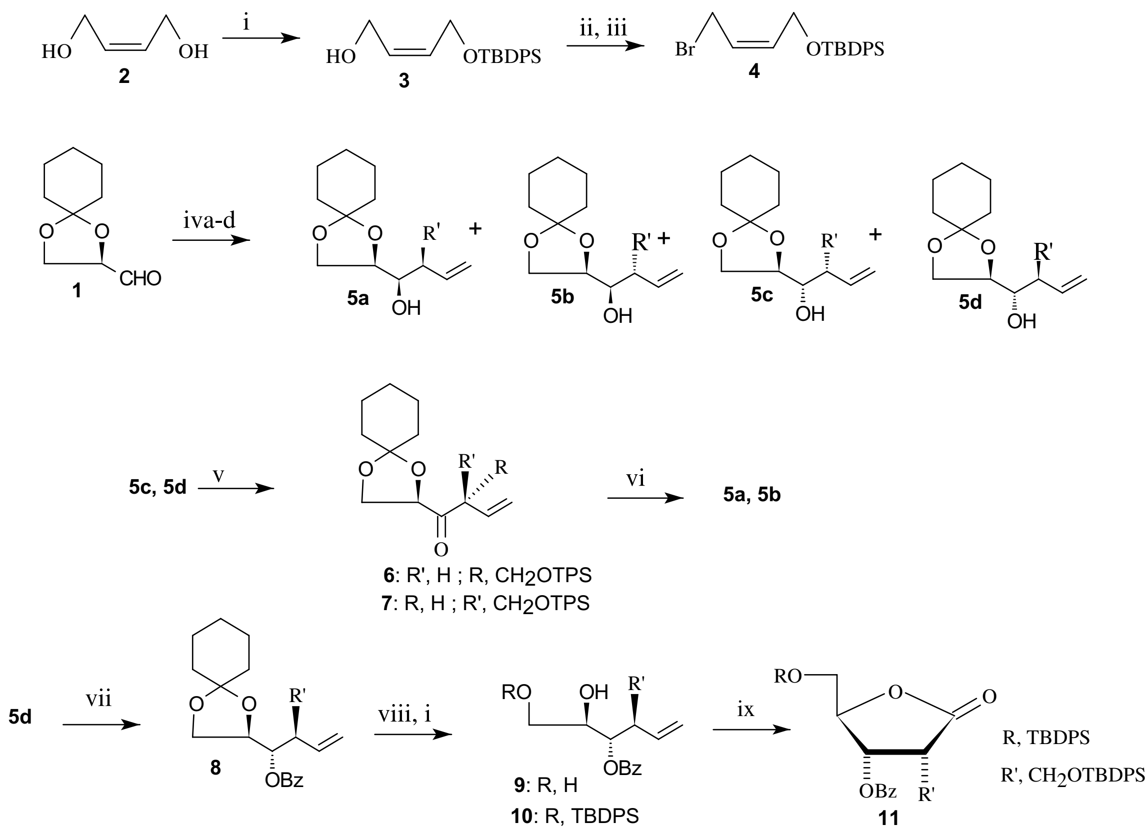
From a mechanistic viewpoint, very high 4,5-*anti* selectivity in all the cases suggests that all the crotylations took place predominantly via a Felkin Anh model,[19] thereby reducing the possibility of α-chelate attack which was apparently not favored due to hydration of metals in the moist reaction environment. Interestingly, of the four cases, copper-mediated addition produced a higher amount of the 3,4-*anti* product. The formation of significant amounts of both 3,4-*syn*- and 3,4-*anti*-products gave ample evidence of a considerable amount of *E*,*Z* equilibration of allylic bromide **6** during carbon–carbon bond formation in all cases.

Benzoylation of **5c** and transformation of the terminal olefin **12** applying boron chemistry[20] afforded primary alcohol **13**. This was oxidized with PCC[21] to give aldehyde **14** in good overall yield. Debenzoylation of **14** under alkaline conditions directly produced furanose **15** possessing a protected hydroxymethyl at the 3-C position. This was acetylated to produce the acetate **16**.[22] Finally, coupling of the latter with silylated thymine following a reported procedure[7a] furnished the corresponding 3′-C branched nucleoside **17**.[23] (Scheme 2). Compound **17**, rather than a hydroxymethyl functionality at C′-5 as observed normally, has a functionalized chiral substituent comprising a primary and a secondary hydroxyl which are suitable for versatile chemical and stereochemical manoeuvres independently of each other.

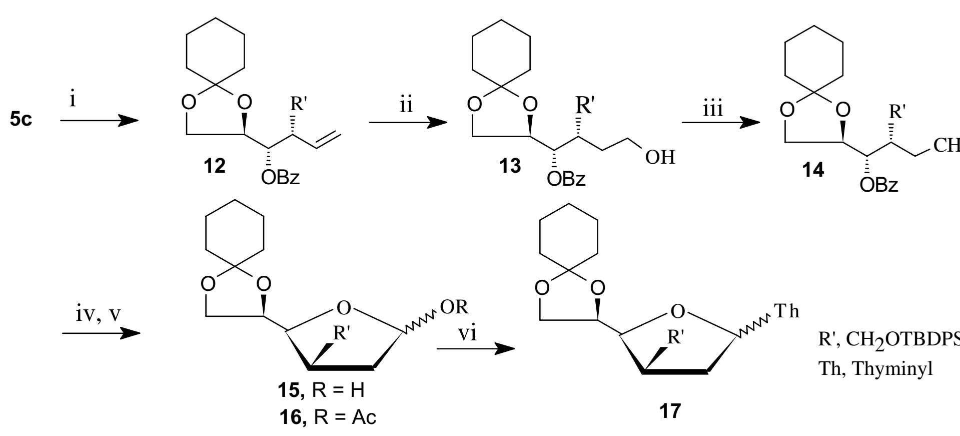
Thus, a very simple, efficient and stereochemically flexible strategy for the synthesis of 3′-C branched 2′,3′-dideoxynucleosides was established through judicious

Table 1. Metal mediated addition of **4** to (*R*)-2,3-cyclohexylideneglyceraldehyde **1**

Entry	Metal/salt	Solvent	**1**:Zn:Metal salt	Reaction time	Product ratio **5a/5b**:**5c**:**5d**	Overall yield (%)
A	Zn/aq NH_4Cl	THF	1:3.5:—	5 h	3:52:45	73
B	Zn/$CoCl_2{\cdot}8H_2O$	THF	1:3.5:3.5	20 h	2:70:28	72.1
C	Zn/$CuCl_2{\cdot}2H_2O$	THF	1:3.5:3.5	20 h	2:33:65	70
D	Zn/$FeCl_3$	THF	1:3:3	30 min	2:50:48	83



Scheme 1. Reagents and conditions: (i) TBDPS-Cl (1 equiv), Im, THF, rt, 77%; (ii) MesCl, TEA; (iii) NaBr, acetone, 86% (two steps); (iva) Zn, aq NH_4Cl, THF; (ivb) $CoCl_2{\cdot}8H_2O$, Zn, THF, rt; (ivc) $CuCl_2{\cdot}2H_2O$, Zn, THF, rt; (ivd) $FeCl_3$, Zn, THF, rt; (v) PCC, CH_2Cl_2, rt, 73%; (vi) K-selectride, THF, −78 °C, 93%; (vii) BzCl, Py, 0 °C, 95%; (viii) CF_3CO_2H, H_2O, 0 °C, 87%; (ix) O_3, MeOH, NaOH, −15 °C, 72%.



Scheme 2. Reagents and conditions: (i) BzCl, Py, 0 °C, 95%; (ii) $Me_2S–BH_3$, hexane, H_2O_2–NaOH, 90%; (iii) PCC, CH_2Cl_2, 71%; (iv) K_2CO_3, MeOH, rt, 75%; (v) Ac_2O, Py, 90%; (vi) thymine, HMDS, NH_4SO_4; TMSOTf, CH_2Cl_2, 72%.

exploitation of easily available **1** and **2**. To establish the viability of our strategy, compound **17** was synthesized as a representative target molecule. In this context, a practically viable method for crotylation of aldehydes has been developed and applied successfully for the reaction between **1** and **4**. This new procedure could be of considerable significance in view of the current attention on crotylation of aldehydes,[24] a valuable alternative to aldol reactions and having versatile synthetic application. The stability of the cyclohexylidene moiety in **1** allowed all these metal-mediated crotylations to be performed simply by stirring under somewhat moist conditions in the presence of metal salts (Table 1, entries b and c). Moreover, the bulky ketal moiety was responsible for the stereoselective conversion of **5c/d** to **5a/b** via an oxidation–reduction protocol.[14] With hindsight, the poor 3,4-stereoselectivity for all these crotylation reactions **1** has ultimately been exploited to our advantage to have access to all four diastereomers **5a–d** starting from the same combination of substrates **1** and **2**. Our strategy was established by exploiting **5c** as a representative precursor to produce nucleoside **17**. Employing a similar strategy, the other stereochemical variations at C-3 and C-4 in the sugar units could be introduced starting from **5a**,**b**,**d**.

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10. Compound **5c**: $[\alpha]_D^{25}$ 20.75 (*c* 1.6, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 1.07 (s, 9H), 1.4 (m, 2H), 1.56–1.62 (m, 8H), 2.26 (m, 1H), 3.02 (br s, 1H), 3.81 (dd, $J = 10.0$, 4.1 Hz, 1H), 3.88–4.0 (m, 5H), 5.0–5.2 (m, 2H), 5.8–6.0 (m, 1H), 7.41 (m, 6H), 7.68 (m, 4H). Anal. Calcd for $C_{29}H_{40}O_4Si$: C, 72.46; H, 8.39. Found, C, 72.29; H, 8.64.
11. Compound **5d**: $[\alpha]_D^{25} - 4.68$ (*c* 1.8, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 1.05 (s, 9H), 1.4 (m, 2H), 1.55–1.62 (m, 8H), 2.53 (m, 1H), 2.84 (br s, 1H), 3.84 (m, 2H), 3.9–4.0 (m, 4H), 5.1–5.2 (m, 2H), 5.7–6.0 (m, 1H), 7.41 (m, 6H), 7.66 (m, 4H). Anal. Calcd for $C_{29}H_{40}O_4Si$: C, 72.46; H, 8.39. Found, C, 72.69; H, 8.61.
12. To a well stirred mixture of **1** (0.01 mol), **4** (0.012 mol) and metal salt [$CoCl_2 \cdot 6H_2O$ (8.4 g, 0.035 mol) or $CuCl_2 \cdot 2H_2O$ (6.0 g, 0.035 mol) or $FeCl_3$ (4.9 g, 0.03 mol)] in THF (70 mL) was added Zn dust (2.25 g, 0.035 mol for Co and Cu; 1.95 g, 0.03 mol for Fe) in portions over a period of 15 min. The mixture was stirred at ambient temperature for the period as shown in Table 1. The reaction mixture was then treated successively with water (50 mL) and EtOAc (100 mL), stirred for 10 min more and then filtered. The filtrate was treated with 2% aqueous HCl to dissolve a small amount of suspended particles. The organic layer was separated. The aqueous layer was extracted with EtOAc. The combined organic layer was washed with water, brine and then dried. Solvent removal and column chromatography of the residue (silica gel, 0–15% EtOAc in petroleum ether) afforded **5a/5b** as an inseparable mixture, and **5c** and **5d** in pure form.
13. The partial (Co and Cu) to good (Fe) solubility of the metal salts in distilled THF which always contains some moisture, plays a role in facilitating bimetal redox reactions and subsequent crotylation. It has been observed, that in anhydrous THF no crotylation reaction took place presumably due to the very poor solubility of these metal salts.
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15. Compound **5a**: $[\alpha]_D^{25} - 2.0$ (*c* 0.9, $CHCl_3$); ^1H NMR(200 MHz, $CDCl_3$): δ 1.04 (s, 9H), 1.4 (m, 2H), 1.55–1.62 (m, 8H), 2.25–2.5 (m, 1H), 2.84 (br s, 1H), 3.6–3.7 (m, 1H), 3.75–4.0 (m, 4H), 4.1–4.2 (m, 1H), 5.0–5.2 (m, 2H), 5.7–6.0 (m, 1H), 7.40 (m, 6H), 7.65 (m, 4H). Anal. Calcd for $C_{29}H_{40}O_4Si$: C, 72.46; H, 8.39. Found, C, 72.24; H, 8.11.
16. Compound **5b**: $[\alpha]_D^{25}$ −7.2 (*c* 1.0, $CHCl_3$); ^1H NMR(200 MHz, $CDCl_3$): δ 1.03 (s, 9H), 1.4 (m, 2H), 1.56–1.62 (m, 8H), 1.90 (br s, 1H), 2.2–2.4 (m, 1H), 3.5–4.0 (m, 5H), 4.1–4.2 (m, 1H), 5.0–5.2 (m, 2H), 5.8–6.0 (m, 1H), 7.39 (m, 6H), 7.64 (m, 4H). Anal. Calcd for $C_{29}H_{40}O_4Si$: C, 72.46; H, 8.39. Found, C, 72.68; H, 8.30.
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18. ^1H NMR data of **11** (200 MHz, $CDCl_3$): δ 0.97 (s, 9H), 1.1 (s, 9H), 3.4–3.5 (m, 1H, H-2), 3.9–4.2 (m, 4H, H-5 and $CH_2OTBDPS$ at H-2), 4.63 (m, 1H, H-4), 5.96 (dd, $J = 13.7$ and 2.4 Hz, 1H, H-3), 7.1–7.9 (m, 25H). For $C_{45}H_{50}O_6Si_2$: C, 72.74; H, 6.78. Found, C, 72.96; H, 7.01.
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22. Compound **16**: $[\alpha]_D^{25}$ 2.3 (*c* 1.4, $CHCl_3$; ^1H NMR (200 MHz, $CDCl_3$): 1.05 (s, 9H), 1.4–1.6 (m, 10H), 1.96 and 2.04 (2s, 3H), 2.1–2.3 (m, 2H, H-2), 2.6 (m, 1H, H-3), 3.6–3.8 (m, 2H), 3.9–4.1 (m, 4H), 6.24 (m, 1H, H-1), 7.40 (m, 6H), 7.65 (m, 4H). Anal. Calcd for $C_{31}H_{42}O_6Si$: C, 69.11; H, 7.86. Found, C, 69.29; H, 8.04.

23. Compound **17**: $[\alpha]_D^{25}$ −15.03 (*c* 0.9, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): 1.05 (s, 9H), 1.4–1.7 (m, 10H, overlapped with a s at 1.7, 3H), 1.9–2.6 (m, 3H, H-2′, H-3′), 3.6–4.0 (m, 3H), 4.1–4.3 (m, 2H), 4.45 (m, 1H, H-4′), 6.38 (m, 1H, H-1′), 7.3–7.5 (m, 6H, phenyl), 7.6–7.7 (m, 5H, 4 phenyl and H-6), 8.1 (br s, 1H, NH). Anal. Calcd for $C_{34}H_{44}N_2O_6Si$: C, 67.52; H, 7.33; N, 4.63. Found, C, 67.35; H, 7.54; N, 4.77.
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