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Stereoselective Synthesis of D-Erythrose and D-Threose Derivatives from D-Glyceraldehyde Acetonide and Their Reactions with 1-(Trimethylsilyl)-vinyl Cuprate Reagent. Synthesis of Allitol Hexaacetate

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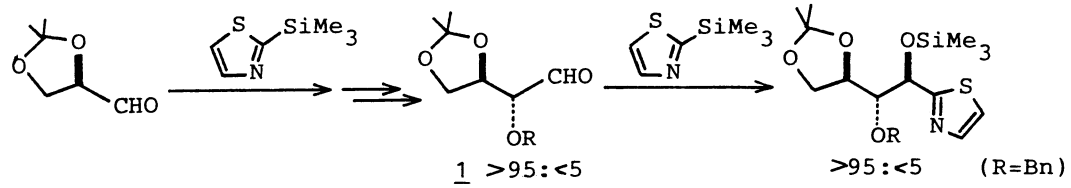
A new and efficient route to the synthesis of trialkoxy derivatives of D-erythrose (1) and D-threose from readily available D-glyceraldehyde acetonide was developed. The addition reaction of 1 with 1-(trimethylsilyl)vinyl cuprate reagent proceeded highly stereoselectively to afford anti addition product, which was then readily converted into allitol hexaacetate.

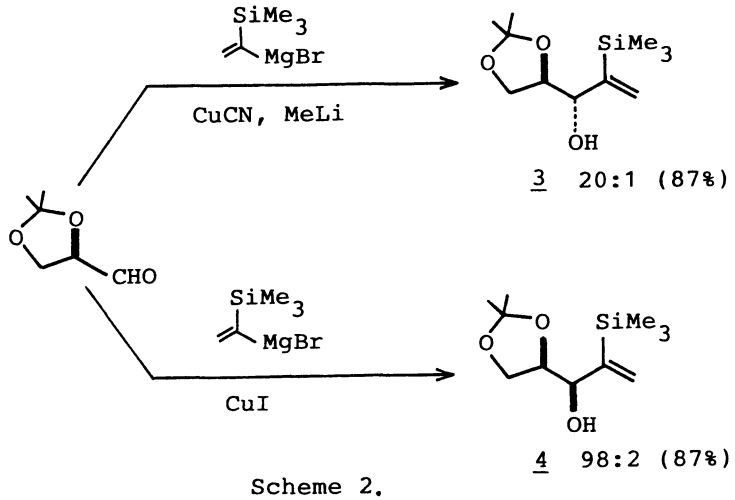
Recently Dondoni and co-workers reported the synthesis of the trialkoxy derivative of D-erythrose (1) from D-glyceraldehyde acetonide and its reaction with 2-(trimethylsilyl)thiazole which proceeded highly stereoselectively to afford anti addition product, a useful chiral building block for synthesizing polyhydroxylated compounds (Scheme 1).[1)]



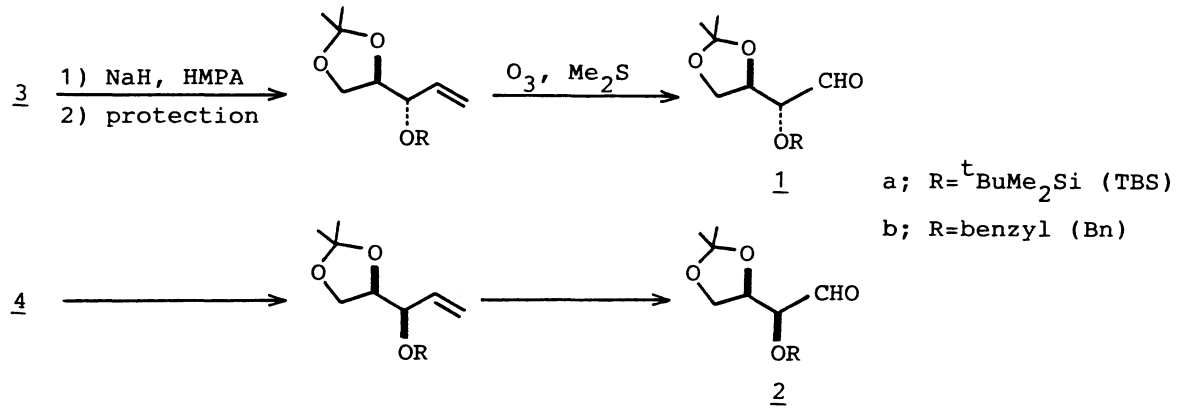
Scheme 1.

Herein we report another convenient route to 1 and also the preparation of its diastereomer D-threose derivative (2) starting with D-glyceraldehyde acetonide. We also report the stereoselective preparation of anti addition product from 1 and 1-(trimethylsilyl)vinyl cuprate reagent and its use to the synthesis of allitol hexaacetate.

It has been recently revealed that the addition reaction of D-glyceraldehyde acetonide with 1-(trimethylsilyl)vinyl cuprate[2)] or 1-(trimethylsilyl)vinyl copper[3)] compounds proceeds highly stereoselectively to afford the anti addition product 3 or the syn addition product 4, respectively, in excellent yields (Scheme 2). The ready availability of 3 and 4 prompted us to convert them into 1 and 2 ,respectively. We succeeded in carrying out this transformation by using a simple sequence of conventional reactions ; 1) protodesilylation with NaH in HMPA,[4)] 2) protection of the hydroxyl group, and 3) ozonolysis. Thus, 1a and 1b were obtained from 3 in 79% and 73% overall



Scheme 2.



Scheme 3.

yield, respectively, and 2a and 2b from 4 in 66% and 77%, respectively (Scheme 3).[5]

With the aldehydes 1 and 2 in hand , we next focused our attention on the addition reaction of these aldehydes with organometallic compounds and found that the reaction of 1-(trimethylsilyl)vinyl cuprate reagent with 1 proceeds highly stereoselectively to afford anti addition product 5 (Eq. 1). Thus, 5a was obtained exclusively in excellent yield from 1a and 1-(trimethylsilyl)vinyl cuprate reagent prepared from 1-(trimethylsilyl)vinyl Grignard reagent, ^{t}BuLi, and CuCN.[6-8] The stereoselectivity is, however, significantly dependent on the bulkiness of the hydroxyl protecting group, and the selectivity was lowered with the reaction of 1b. The anti selectivity in the present reaction can be explained by Felkin-Anh model depicted in Fig. 1. Especially in the case of 1a this conformation must be quite stable because of the bulkiness of TBS group, resulting in exclusive production of 5a. Noteworthy also is the fact that the reaction of 2 (the diastereomer of 1) with 1-(trimethylsilyl)vinyl cuprate reagent proceeds with poor selectivity (Eq. 2), which suggests the stereoselectivity is also affected by the relative stereochemistry of the aldehyde.[9]

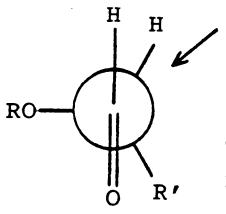
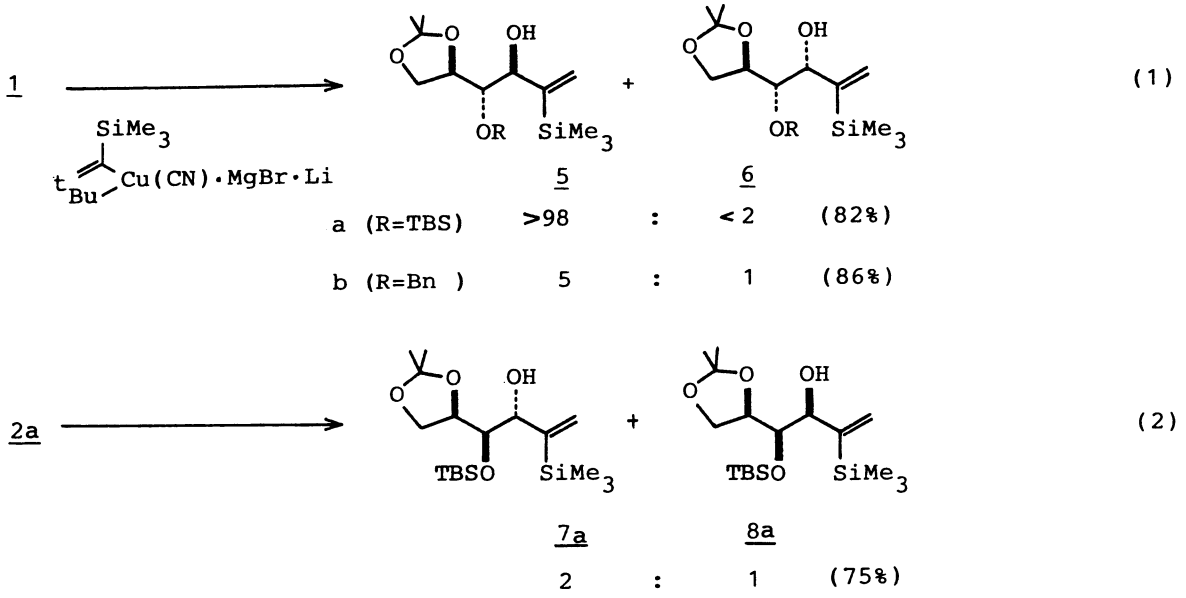
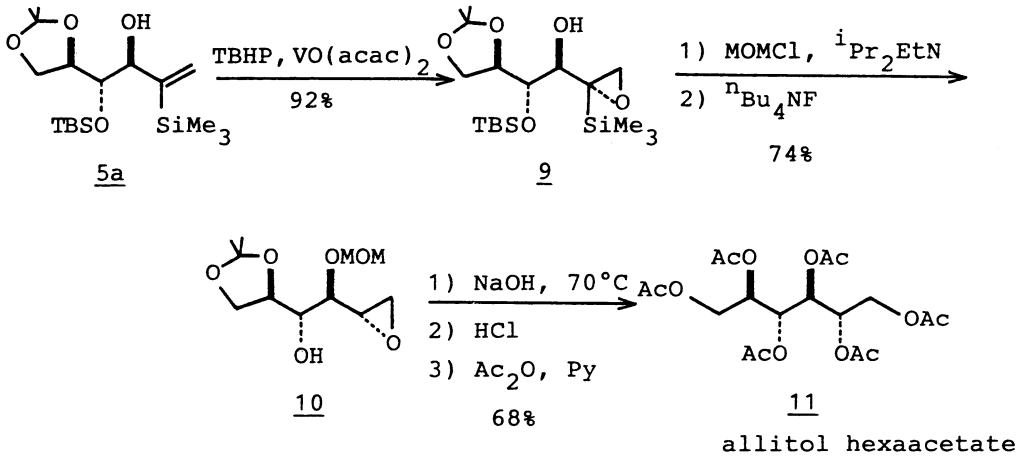


Fig. 1.



In our opinion, 5a thus obtained can serve as a useful precursor for the stereoselective synthesis of sugars which is one of the current topics in organic synthesis.[10] As an example, we converted 5a into allitol hexaacetate as shown in Scheme 4. Epoxidation of 5a using TBHP-$VO(acac)_2$ afforded 9 exclusively in 92% yield.[11,12] After protection of the hydroxyl group with methoxymethyl group (MOMCl-$^{i}Pr_2EtN$), two silyl groups were removed by treatment with $^{n}Bu_4NF$ to give 10[12] (74%). The resulting compound 10 was readily converted into allitol hexaacetate (11)[12] according to the procedure reported by Masamune and Sharpless.[13]



Scheme 4.

References

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2) M. Kusakabe, and F. Sato, J. Chem. Soc., Chem. Commun., in press.
3) F. Sato, Y. Kobayashi, O. Takahashi, T. Chiba, Y. Takeda, and M. Kusakabe,

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5) 1b; 1H NMR data were in accord with values reported by Dondoni.[1]; $[\alpha]_D^{25}$ +35.3° (c 1.30, $CHCl_3$). 2b; ^1H NMR (CCl_4) δ 1.26 and 1.33 (2s, 6H), 3.68 (dd, J = 1.4, 4.9 Hz, 1H), 3.76-4.36 (m, 3H), 4.56 and 4.67 (2d, J = 12 Hz, 2H), 6.97-7.40 (m, 5H), 9.59 (d, J = 1.4 Hz, 1H); $[\alpha]_D^{25}$ -25.0° (c 1.21, $CHCl_3$).

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7) Experimental procedure for the preparation of 5a is as follows.
To a suspension of CuCN (242 mg, 2.70 mmol) in THF (6 ml) were added 1-(trimethylsilyl)vinyl Grignard reagent (5.29 ml, 0.51 M in THF, 2.70 mmol) and then ^{t}BuLi (1.35 ml, 2.00 M in pentane, 2.70 mmol) at -50 °C. After 5 min, the solution was cooled down to -78 °C and the solution of 1a (495 mg, 1.80 mmol) in THF (5 ml) was added. The mixture was stirred for 10 min at -78 °C and 1 h at room temperature. Usual workup and purification by column chromatography gave 5a (555 mg, 82%).

8) The compound 5a showed the following data; ^1H NMR (CCl_4) δ 0.13 (s, 15H), 0.89 (s, 9H), 1.17 and 1.28 (2s, 6H), 2.42 (brs, 1H), 3.62-4.16 (m, 4H), 4.23-4.41 (m, 1H), 5.40-5.54 (m, 1H), 5.83-6.00 (m, 1H); ^{13}C NMR ($CDCl_3$) δ -4.6, -4.3, -0.8, 18.0, 25.5, 25.8, 26.4, 64.2, 73.0, 74.9, 76.3, 107.0, 125.0, 149.1; IR (nujol) 3500, 1250, 835 cm^{-1}; $[\alpha]_D^{25}$ + 24.1° (c 1.06, $CHCl_3$).

9) The reaction of 1 and 2 with 1-(trimethylsilyl)vinyl copper reagent prepared from 1-(trimethylsilyl)vinyl Grignard reagent and CuI which we expected to afford syn addition product 6[3] resulted in complete recovery of the starting aldehydes. The reaction with 1-trimethylsilyl Grignard reagent resulted in poor stereoselectivity.

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11) H. Tomioka, T. Suzuki, K. Ohshima, and H. Nozaki, Tetrahedron Lett., 23, 3387 (1982). A. S. Narula, ibid., 23, 5579 (1982).

12) 9; ^1H NMR (CCl_4, D_2O) δ 0.09 (s, 15H), 0.84 (s, 9H), 1.20 and 1.27 (2s, 6H), 2.46 and 2.93 (2d, J = 4.9 Hz, 2H), 3.66-4.13 (m, 5H); ^{13}C NMR ($CDCl_3$) δ -4.5, -3.0, 18.0, 25.4, 25.7, 26.4, 46.5, 51.6, 65.9, 72.4, 72.8, 75.1, 107.7; IR (nujol) 3430, 1245, 835 cm^{-1}; $[\alpha]_D^{25}$ +24.5° (c 1.03, $CHCl_3$). 10; ^1H NMR (CCl_4, D_2O) δ 1.28 and 1.34 (2s, 6H), 2.51-2.76 (m, 2H), 2.99-3.16 (m, 1H), 3.31 (s, 3H), 3.52 (dd, J = 2.9, 5.3 Hz, 1H), 3.70 (dd, J = 3.0, 6.7 Hz, 1H), 3.83-4.25 (m, 3H), 4.55 and 4.57 (2d, J = 5.4 Hz, 2H); IR (neat) 3440, 1210, 1025 cm^{-1}; $[\alpha]_D^{25}$ +24.7° (c 1.19, $CHCl_3$). 11; ^1H NMR ($CDCl_3$) δ 2.03 (s, 6H), 2.055 (s, 6H), 2.06 (s, 6H), 4.15 (dd, J = 5.8, 12.3 Hz, 2H), 4.32 (dd, J = 2.7, 12.3 Hz, 2H), 5.12-5.46 (m, 4H); $[\alpha]_D^{25}$ 0° (c 0.51, EtOH).

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