Table 3. Structural Data of 1,3-Dithiolan-2-ylidenemalonate Analogs

Compound*	S···O distance (Å)	C=C distance (Å)	Dihedral angle(°) between two carboxylates	Ref.
K-salt	3.37 2.74	1.347(6)	83.6	This work
Me-ester	2.80 2.70	1.365(5)	48.1	3
Pt-complex	2.53 2.55	1.374(9)	14.5	1

*K-salt: Potassium 1,3-dithiolan-2-ylidenemalonate. Me-ester: Dimethyl 1,3-dithiolan-2-ylidenemalonate. Pt-complex: *cis*-Bis(cyclopropylamine)(1,3-dithiolan-2-ylidenemalonato)platinum(II)

oxygen interactions is linearly consistent with the trend of the dihedral angles between two carboxylates and the C=C bond lengths. Such prominent differences of the structural data among the compounds indicate that the presence of two anions strongly affects structural environment of these species of compounds.

In conclusion, the conformation of the two carboxylate groups of a dicarboxylate ligand seems to be dependent on their bonding nature, and for the title potassium salt, the characteristic properties such as perpendicular conformation of two carboxylates, C=C bond length, and S···O distance may be ascribed to domination of the electrostatic repulsion of the two adjacent anionic carboxylate groups in the molecular structure.

Acknowledgment. We acknowledge the financial support of this research by the Ministry of Science and Technology in Korea.

References

1. Lee, S. S.; Jun, M.-J.; Kim, K. M.; Jung, O.-S.; Sohn, Y. S. *Polyhedron* **1994**, *13*, 1397.
2. Sohn, Y. S.; Kim, K. W.; Kang, S. J.; Jung, O.-S. *Inorg. Chem.* in press.
3. Kim, K. M.; Lee, Y.-A.; Jung, O.-S.; Sohn, Y. S. *Bull. Korean Chem. Soc.* **1996**, *17*, 93.
4. Katagiri, N.; Ise, S.; Watanabe, N.; Kaneko, C. *Chem. Pharm. Bull.* **1990**, *38*, 3242.
5. (a) Sheldrick, G. M. SHELXS-86: A Program for Structure Determination; University of Gottingen, Germany, 1986. (b) Sheldrick, G. M. SHELXL-93: A Program for Structure Refinement; University of Gottingen, Germany, 1993.
6. Allen, F. H.; Kennard, O.; Watson, D. G. *J. Chem. Soc., Perkin Trans. II.* **1987**, S1.

Catalytic Redistribution/Dehydrocoupling of 2-Phenyl-1,3-disilapropane by Cp_2MCl_2/Red-Al System (M=Ti, Hf)

Hee-Gweon Woo*, Sun-Jung Song, Hyun You,
Eun Jeong Cho†, and Il Nam Jung†

Department of Chemistry,
Chonnam National University,
Kwangju 500-757, Korea
†Organometallic Chemistry Laboratory,
Korea Institute of Science & Technology,
P.O. Box 131 Cheongryang,
Seoul 130-650, Korea

Received January 29, 1996

Polysilanes with unusual optical and electronic properties due to σ-conjugation along the silicon backbone have been used for many special applications such as ceramic precursors, third-order NLO materials, deep-UV photoresists, photoconductors, and photoinitiators.[1] The conventional synthetic method to currently get high-molecular-weight polysilanes has been the Wurtz coupling reaction of dichlorosilanes using alkali metals, which is intolerant of some functional groups, lack of reproducibility, and have some limitations for controlling stereochemistry and molecular weight.

Harrod's recent discovery of group 4 metallocene-catalyzed dehydropolymerization led to great progress in poly(organosilane) synthesis.[2] A major handicap of the metallocene-catalyzed dehydrocoupling method is the production of low-molecular-weight polysilanes.[2,3] Intensive efforts have been made to increase the molecular weight of the polysilanes.[4~8]

Tilley *et al.* reported the dehydropolymerization of bis- and tris(silyl)arenes to produce highly cross-linked polysilanes.[4] We recently reported the dehydropolymerization of 2-phenyl-1,3-disilapropane, **1** to highly cross-linked polysilanes catalyzed by Cp_2MCl_2/*n*-BuLi (M=Ti, Hf).[5] We very recently described the catalytic redistribution of **1** by Red-Al.[10] Here we wish to report the catalytic dehydrocoupling of **1** by Cp_2MCl_2/Red-Al (M=Ti, Hf) yielding a low-molecular-weight polymer to compare with the dehydrocoupling of **1** by Cp_2MCl_2/*n*-BuLi (M=Ti, Hf).

Experimental Section

General Considerations. All reactions and manipulations were performed under prepurified nitrogen using Schlenk techniques. Dry, oxygen-free solvents were employed throughout. Glassware was flame-dried or oven-dried before use. Infrared spectra were obtained using a Perkin-Elmer 1600 series FT-IR or a Nicolet 520P FT-IR spectrometer. Proton NMR spectra were recorded on a Varian Gemini 300 spectrometer using $CDCl_3/CHCl_3$ as a reference at 7.24 ppm downfield from TMS. Gas chromatography (GC) analyses were performed using a Varian 3300 chromatograph equipped with a packed column (10% OV-101 on Chromosorb, W/AW-DMCS 1.5 m×1/8″ in. o.d.) in conjunction with a flame ionization detector. GC/MS data were obtained using a Hewlett-Packard 5890II chromatograph (HP-5, 5% phenylmethylsiloxane, 0.25 mm i.d.×30.0 m, film thickness 0.25 μm) connected to a Hewlett-Packard 5972A mass selective detector. Gel permeation chromatography (GPC) was carried out on a Waters Millipore GPC liquid chromatograph. The calibrant (monodisperse polystyrene) and the sample were dissolved in toluene and separately eluted from an Ultrastyragel GPC column series (sequence 500, 10^3, 10^4 Å columns). Molecular weights were extrapolated from the calibration curve derived from the polystyrene standard. Data analyses were carried out using a Waters Data Module 570. Thermogravimetric analysis (TGA) of the polymer sample was performed on a Perkin-Elmer 7 Series thermal analysis system under an argon flow. The polymer sample was heated from 25 to 800 ℃ at a rate of 20 ℃/min. Ceramic residue yield is reported as the percentage of the sample remaining after completion of the heating cycle. Cp_2TiCl_2, Cp_2HfCl_2, and Red-Al (3.4 M in toluene) were purchased from Aldrich Chemical Co. and were used without further purification. 2,3-Dimethyl-1,3-butadiene, cyclohexene, and trimethylmethoxysilane (Aldrich Chemical Co.) were purified before use according to the known purification method.[11] **1** was prepared according to the literature procedure.[9]

Dehydrocoupling of 1 Catalyzed by Cp_2TiCl_2/Red-Al. To a Schlenk flask loaded with Cp_2TiCl_2 (2.5 mg, 0.01 mmol) and Red-Al (3.0 μL, 0.01 mmol) was added slowly **1** (0.38 g, 2.5 mmol). (*Warning! The addition order, addition rate, and catalyst concentration should be obeyed. Otherwise, a violent explosion with fire will be resulted due to the drastic production of SiH_4 which is an explosive gas upon contact with air. Therefore, the reaction should be performed with suitable precaution. We recommend you not to exceed the reaction scale employed here.*) The reaction mixture immediately turned dark green, and the reaction medium became viscous with vigorous gas evolution. After 8 h, the catalyst was deactivated by exposure to the air. The low-boiling products were isolated by bulb-to-bulb vacuum distillation. The remaining high-boiling mixture was passed rapidly through a reverse phase silica gel column (70-230 mesh, 20 cm×2 cm) with 200 mL of toluene used as the eluent. The colorless effluent was evaporated to dryness to yield 0.06 g (20% yield) of a viscous opaque oil which was soluble in most organic solvents. IR (neat, KBr, cm^{-1}): 3022 w, 2922 m, 2852 w (ν_{CH}), 2148 s (ν_{SiH}), 1594 w, 1492 m, 1450 w, 1032 m, 922 s (δ_{SiH}), 878 m, 696 s. ^1H NMR (δ, $CDCl_3$, 300 MHz): 1.2-2.5 (m, CH), 3.6-4.4 (m, SiH), 6.5-7.5 (m, ArH); GPC: $\bar{M}_w=550$, $\bar{M}_n=350$. TGA ceramic residue yield 2% (black solid).

Identification of Low-boiling Products. The low-boiling products above obtained were subject to GC/MS analysis. The low-boiling products were identified to be benzylsilane (3%), dibenzylsilane (2%), 2,4-diphenyl-1,3-disilabutane (7%), 2,4-diphenyl-1,3,5-trisilapentane (61%), 2,5-diphenyl-1,3,4,6-tetrasilahexane (8%), and unidentified products (19%).

Benzylsilane (2). GC/MS (m/e, relative intensity) 122 (32) (M^+), 105 (4), 91 (100), 65 (14), 53 (6).

Dibenzylsilane (3). GC/MS (m/e, relative intensity) 212 (24) (M^+), 121 (100), 105 (8), 91 (18), 65 (8), 53 (4).

2,4-Diphenyl-1,3-disilabutane (4). GC/MS (m/e, relative intensity) 242 (30) (M^+), 210 (6), 151 (72), 121 (89), 120 (100), 105 (38), 91 (33), 65 (10), 53 (12).

2,4-Diphenyl-1,3,5-trisilapentane (5). GC/MS (m/e, relative intensity) 272 (35) (M^+), 237 (4), 235 (6), 181 (16), 151 (100), 149 (61), 120 (86), 105 (42), 81 (4), 67 (8), 53 (12). ^1H NMR (δ, $CDCl_3$, 300 MHz): 1.82 (h, 1H, $J=2.2$ Hz, CH), 1.89 (h, 1H, $J=2.2$, CH), 3.73 (d, 6H, $J=2.2$ Hz, SiH_3), 3.75 (d, 6H, $J=2.2$ Hz, SiH_3), 4.19-4.26 (m, 2H, SiH_2), 6.9-7.3 (m, 10H, ArH).

2,4-Diphenyl-1,3,4,6-tetrasilahexane (6). GC/MS (m/e, relative intensity) 302 (1) (M^+), 181 (100), 149 (23), 119 (26), 105 (16), 93 (10), 69 (3), 53 (4).

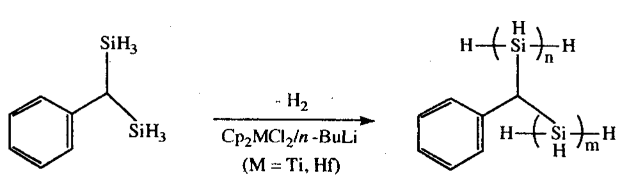
Dehydrocoupling of 1 Catalyzed by Cp_2TiCl_2/Red-Al in the Presence of a Trapping Agent. To a Schlenk flask charged with Cp_2TiCl_2 (5.0 mg, 0.02 mmol), Red-Al (6.0 μL, 0.02 mmol), and 2,3-dimethyl-1,3-butadiene (4.0 mL, 35 mmol) was injected slowly **1** (0.304 g, 2.0 mmol). The reaction mixture immediately turned dark green, and the reaction medium became viscous with mild gas evolution. After 3 h, the catalyst was allowed to oxidize by exposure to the air. The low-boiling products were isolated by bulb-to-bulb vacuum distillation. The resulting low-boiling products were analyzed by GC/MS. The analyses showed the presence of **2** (27%), **4** (7%), **5** (63%), and **6** (3%). Cyclohexene and trimethylmethoxysilane showed the similar results as 2,3-dimethyl-1,3-butadiene.

Dehydrocoupling of 1 Catalyzed by Cp_2HfCl_2/Red-Al. **1** (2.0 g, 13.2 mmol) was drop by drop added to a Schlenk flask loaded with Cp_2HfCl_2 (20.0 mg, 0.053 mmol) and Red-Al (17.0 μL, 0.058 mmol). (*Warning! The addition order, addition rate, and catalyst concentration should be obeyed as described in the catalytic dehydrocoupling by Cp_2TiCl_2/Red-Al.*) The reaction mixture immediately turned light yellow, and the reaction medium became viscous with rapid gas evolution. After 2 h, the mixture was heated 90 ℃ for 5 h. The catalyst was destroyed by exposure to the air. The crude mixture was passed rapidly through a reverse phase silica gel column (70-230 mesh, 20 cm×2 cm). The column was rinsed with 200 mL of toluene. The removal of volatiles at reduced pressure yielded 0.56 g (28% yield) of a very viscous opaque oil which was soluble in most organic solvents. IR (neat, KBr, cm^{-1}): 3022 w, 2922 m, 2852 w (ν_{CH}), 2148 s (ν_{SiH}), 1594 w, 1492 m, 1450 w, 1032 m, 922 s (δ_{SiH}), 878 m, 696 s. ^1H NMR (δ, $CDCl_3$, 300 MHz): 1.2-2.5 (m, CH), 3.6-4.4 (m, SiH), 6.5-7.5 (m, ArH); GPC: $\bar{M}_w=2040$, $\bar{M}_n=770$. TGA ceramic residue yield 3% (black solid).

Results and Discussion

Although Cp_2MMe_2 (M=Ti, Zr),[2] $Cp_2Zr[Si(SiMe_3)_3]Me$,[3a~e] and Cp_2ZrCl_2/*n*-BuLi[12] are known to be the active catalysts for the dehydropolymerization of primary silanes and $CpCp^*Zr[Si(SiMe_3)_3]Me$ and $(CpCp^*ZrH_2)_2$ were the most active catalyst previously examined,[3a~e] we wanted to employ a novel catalyst system, Cp_2MCl_2/Red-Al (M=Ti, Hf),[13] which was recently found to give predominantly linear, higher molecular weight of polysilanes than for any other catalyst system. We first expected that the catalytic dehydrocoupling of **1** by Cp_2MCl_2/*n*-BuLi and Cp_2MCl_2/Red-Al (M=Ti, Hf) catalyst systems could give the same type of polysilane because both catalyst systems are known to produce same catalytic species in the presence of silane,[3,7,12] but they gave totally different products (*vide infra*).

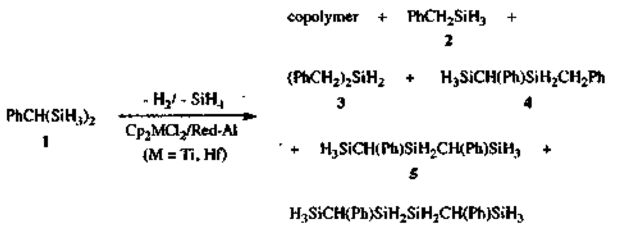
We reported earlier that dehydrocoupling of **1** with the Cp_2MCl_2/*n*-BuLi(M=Ti, Hf) catalyst system produced two phases of polymers in >90% total yield after workup including washing and column chromatography (eq. 1).[9]



1 (1)

Insoluble solid polymers were obtained in 82% yield for Ti and in 80% yield for Hf. The TGA ceramic residue yield of the insoluble solid polymers was 72% for Ti and 74% for Hf. Soluble oily polymers were acquired in 13% yield for Ti and in 14% yield for Hf. A study on the bulk pyrolyses of the polymers are in progress and will be reported in the future. The weight average molecular weight ($\bar{M}_w$) and number average molecular weight ($\bar{M}_n$) of the oily polymers were 4120 and 820 for Ti and 5010 and 850 for Hf. The ^1H NMR spectra of the soluble polysilanes showed nearly one broad unresolved mountain-like peaks centered at *ca.* 4.0 ppm assigned to the Si-H resonances. The IR spectra of all the polysilanes exhibited an intense ν_{Si-H} band in around 2110 cm^{-1}. We found from the results that the expected polysilanes were obtained from the dehydrocoupling of **1** with Cp_2MCl_2/*n*-BuLi catalyst system without redistribution of **1**.[9] By contrast, present catalytic reaction of **1** with the Cp_2MCl_2/Red-Al (M=Ti, Hf) catalyst system yields a complex mixture of products by both redistribution and dehydrocoupling reactions of **1**.

Redistribution/dehydrocoupling of **1** with the Cp_2TiCl_2/Red-Al catalyst system commenced immediately and the reaction medium became slowly viscous (eq. 2).

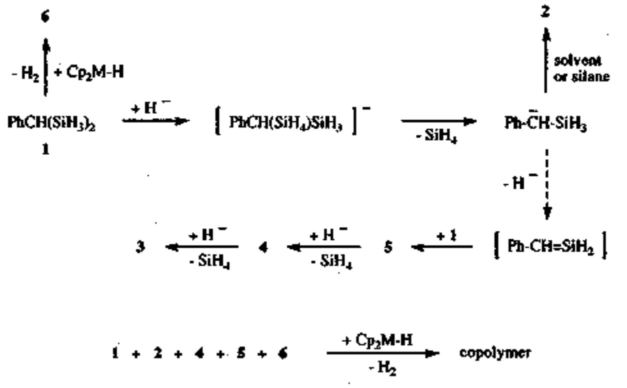


(2)

Redistribution/dehydrocoupling of **1** with the Cp_2HfCl_2/Red-Al catalyst system was occurred at a slow rate and the reaction medium became rapidly viscous upon being heated at 90 ℃. The polymer was obtained in 20% yield for Ti and 28% yield for Hf as a viscous opaque oil after workup including column chromatography. The TGA ceramic residue yield of the polymers was 2% for Ti and 3% for Hf. The weight average molecular weight and number average molecular weight of the polymers were 550 and 350 for Ti and 2040 and 770 for Hf. The ^1H NMR spectra of the polysilanes apparently show broad unresolved mountain-like peaks in the region of 3.6-4.4 ppm assigned to the Si-H resonances. The IR spectra of the polysilanes show an intense ν_{Si-H} band in around 2148 cm^{-1}.

Although enough experimental data are not currently available, some comments on the catalytic redistribution/dehydrocoupling mechanism of **1** by Cp_2MCl_2/Red-Al seem appropriate. We propose a mechanism involving the preferential attack of the hydride on the less hindered silicon with formation of a pentacoordinated anionic species which collapses to give an α-silyl carbanion intermediate and SiH_4 gas. The α-sily carbanion may then pick up a hydrogen from the hydrogen source (e.g., silane or solvent) to yield **2** or may lose a hydride participating again in the catalytic cycle to produce phenylsilene. Experiments for trapping silene using 2,3-dimethyl-1,3-butadiene, cyclohexene, and trimethylmethoxysilane were unsuccessful due probably to the hydrosilanes possessing active Si-H bonds abundantly existed in the reaction mixture. **1** may add to the phenylsilene to give **5** which will become **3** and **4** by sequentially losing SiH_4 gas. The silanes might then undergo catalytic dehydrocoupling to yield a copolymer (Scheme 1).

We tentatively assign the polymer as a copolymer. We are making our effort to elucidate the structure of the copolymer using ^{13}C and ^{29}Si NMR spectroscopy. One may note that the redistribution of **1** could only occur prior to the dehydrocoupling when Cp_2MCl_2/Red-Al used as a catalyst, but the dehydrocoupling could occur without redistribution when Cp_2MCl_2/*n*-BuLi used as a catalyst. This provides an example of forming different types of polymers, depending on the combination of same metallocene with the different anionic additive. The silane **3** could hardly undergo dehydrocoupling because of its steric bulkiness. In addition, the secondary silyl groups in the silanes **4-6** seldom undergo dehydrocoupling due to their steric bulkiness. The dehydrocoupling reactivity of hydrosilanes is known to decrease drastically in the order primary>sencondary>tertiary.[3,5] The two silyl groups of **1** should independently participate in the dehydrocoupling to produce a cross-linked insoluble polymer with Cp_2MCl_2/*n*-BuLi. If two silyl groups of **1** dependently partake in the dehydrocoupling, it could produce an uncross-linked soluble polymer. One might naturally think that the dehydrocoupling of **1** with Cp_2MCl_2/*n*-BuLi first produced a low-molecular-weight polymer which then underwent an extensive cross-linking reaction of backbone Si-H bonds, leading to an insoluble polymer. The detailed study on the different behaviour



Scheme 1. Postulated mechanism for catalytic redistribution/dehydrocoupling of **1** by Cp_2MCl_2 (M=Ti, Hf)/Red-Al.

of two catalyst systems are in progress and will be reported in the future.

In conclusion, this work describes the catalytic redistribution/dehydrocoupling of 2-phenyl-1,3-disilapropane by Cp_2MCl_2/Red-Al (M=Ti, Zr, Hf). Unlike Cp_2MCl_2/*n*-BuLi (M=Ti, Hf) catalyst system yielding a cross-linked insouble polymer via simple dehydrocoupling process, the Cp_2MCl_2/Red-Al catalyst system produced an uncross-linked soluble polymer *via* redistribution/dehydrocoupling process. A plausible mechanism for the formation of soluble polymers was provided.

Acknowledgment. This research was supported by the Non-directed Research Fund, Korea Research Foundation (1995).

References

1. (a) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359. (b) West, R. *J. Organomet. Chem.* **1986**, *300*, 327. (c) Ziegler, J. M.; Fearon, F. W. G. *Silicon-based Polymer Science*; American Chemical Society: Washington, DC, 1990.
2. (a) Aitken, C.; Harrod, J. F.; Gill, U. S. *Can. J. Chem.* **1987**, *65*, 1804. (b) Harrod, J. F.; Yun, S. S. *Organometallics* **1987**, *6*, 1381. (c) Aitken, C.; Barry, J.-P.; Gauvin, F.; Harrod, J. F.; Malek, A.; Rousseau, D. *Organometallics* **1989**, *8*, 1732. (d) Harrod, J. F.; Ziegler, T.; Tschinke, V. *Organometallics* **1990**, *9*, 897. (e) Woo, H.-G.; Harrod, J. F.; Hénique, J.; Samuel, E. *Organometallics* **1993**, *12*, 2883. (f) Britten, J.; Mu, Y.; Harrod, J. F.; Polowin, J.; Baird, M. C.; Samuel, E. *Organometallics* **1993**, *12*, 2672.
3. (a) Woo, H.-G.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 3757. (b) Woo, H.-G.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 8043. (c) Woo, H.-G.; Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 5698. (d) Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 7047. (e) Banovetz, J. P.; Suzuki, H.; Waymouth, R. M. *Organometallics* **1993**, *12*, 4700. (f) Campbell, W. H.; Hilty, T. K. *Organometallics* **1989**, *8*, 2615.
4. (a) Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *Macromolecules* **1991**, *24*, 6863. (b) Imori, T.; Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *Chem. Mater.* **1993**, *5*, 1487.
5. (a) Harrod, J. F. In *Transformation of Organometallics into Common and Exotic Materials: Design and Activation*; Laine, R. M., Ed.; NATO ASI Series E.: Appl. Sci. no. 141; Martinus Nijhoff Publishers: Amsterdam, 1988; p 103. (b) Mu, Y.; Harrod, J. F. In *Inorganic and Organometallic Polymers and Oligomers*; Harrod, J. F., Laine, R. M., Eds.; Kluwer Academic Publishers: Dordrecht, 1991; p 23.
6. (a) Dioumaev, V. K.; Harrod, J. F. *Organometallics* **1994**, *13*, 1548. (b) Dioumaev, V. K.; Harrod, J. F. Manuscript in preparation.
7. Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22.
8. (a) Hengge, E.; Weinberger, M.; Jammegg, C. *J. Organomet. Chem.* **1991**, *410*, C1. (b) Hengge, E.; Weinberger, M. *J. Organomet. Chem.* **1992**, *433*, 21.
9. Woo, H.-G.; Kim, S.-Y.; Kim, W.-G.; Yeon, S. H.; Cho, E. J.; Jung, I. N. *Bull. Korean Chem. Soc.* **1995**, *16*, 1109.
10. Woo, H.-G.; Song, S.-J.; Cho, E. J.; Jung, I. N. *Bull. Korean Chem. Soc.* **1996**, *17*, 123.
11. Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; 3rd Ed.; Pergamon: New York, 1989.
12. Corey, J. Y.; Huhmann, J. L.; Zhu, X.-H. *Organometallics* **1993**, *12*, 1121.
13. Woo, H.-G.; Harrod, J. F. Unpublished results.

An Effective Synthesis of 4-*O*-*tert*-Butyldimethylsilyl-2,3-*O*-isopropylidene-L-threose and erythrose: Useful Chiral Building Blocks in Synthesis

Joo Yong Kim, Jeong E. Nam Shin, and Keun Ho Chun*

Department of Chemistry, Soongsil University, Seoul 156-743, Korea

Received February 2, 1996

Polyfunctional building blocks from the chiral pool are highly useful in natural product synthesis. Various mono or oligosaccharides used to be converted into valuable intermediates, chiral synthons, or chiral auxiliaries. Both enantiomers of glyceraldehyde derivatives have been widely applied for those purpose. The chemistry of various pentose, hexose, heptose, and disaccharide like sucrose have been deeply investigated, and their results ensured the value of carbohydrates as organic raw materials.[1]

However, relatively few reports about tetrose have been found in spite of their synthetic potentials. Tetrose: D, L-threose and D, L-erythrose: are classified as rare carbohydrates. Although some of them are accessible in chemical market, they are still expensive materials. Recently, synthetic chemists took their interests in tetrose derivatives, and diverse applications have been published.[2] In general, properly protected derivatives are more useful for synthetic purpose rather than tetrose itself. Because of rareness and high price, most tetrose derivatives have been usually prepared from other raw molecules. D, L-Threose from L-ascorbic acid,[3] D, L-arabinitol,[4] D, L-tartaric acid,[5] L-glyceraldehyde[6] were reported. L-Rhamnose,[7] 6-deoxy-L-mannose,[4] D-gulono-1,4-lactone[8] and D-ribono-1,4-lactone[9] were employed as starting materials for the synthesis of L-erythrose. D-Erythrose derivatives were usually prepared starting from D-erythronolacton.[10]

We needed properly protected all four stereoisomers of tetrose for our alkaloid synthesis. Although reported preparations of individual tetrose derivatives are reasonable enough, it was still inconvenient for us to prepare four stereoisomers through four different synthetic schemes. It was necessary to develop more general and convenient way to get properly protected D, L-threose and erythrose.

Starting from D-xylose (**1**), 4-*O*-*tert*-butyldimethylsilyl-2,3-*O*-isopropylidene-L-threose (**7**) was prepared effectively. When the starting sugar changes to D-lyxose (**8**), with same procedure, 4-*O*-*tert*-butyldimethylsilyl-2,3-*O*-isopropylidene-L-