COMMUNICATIONS TO THE EDITOR

The Synthesis of Spiro Orthocarbonate Based on Catechol

Kwanghyun No

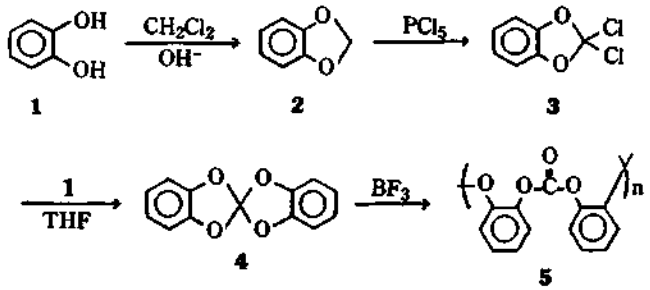
Department of Chemistry, Sookmyung Women's University Seoul 140-132. *Received November 30, 1987*

Monomers that will polymerize with near zero shrinkage or volume expansion are highly desireable for practical applications of polymeric materials, such as strain free composites, precision castings, dental filling and semi-conductor encapsulations.

Spiro orthocarbonate which is a bicyclic compound, was found to expand volume on ring opening polymerization in which for every bond that goes from a Van der Waals' distance to a covalent distance, at least two bonds would go from a covalent distance to a near Van der Waals' distance. Therefore the volume shrinkage on a bond formation can be compensated with the volume expansion on two bonds breakage.

Bailey and coworkers[1,2] reported the preparation of various spiro orthocarbonates and the practical applications such as epoxy resin modifier, dental filling and elastomers. We also reported the preparation of spiro orthocarbonate based on anthracene.[3]

However all of these monomers which have been synthesized contain aliphatic carbons which render them thermally and oxidatively less stable. The totally aromatic spiro orthocarbonate seems to improve these disadvantages. Bailey and coworkers[4] prepared 2,3,7,8-dibenzo-1,4,6,9-tetraoxaspiro-[4,4]nonadiene as following procedures. After the reaction of phosgene with catechol, the resulting orthocarbonate was treated with PCl_5 at 210-220 °C to yield 2,2-dichlorobenzo-1,3-dioxole **3** which was heated with catechol in absolute ether to give spiro orthocarbonate **4** in 46% overall yield from catechol. Due to the interesting aspects of compound **4** as a expanding monomer which has improved thermal and oxidative properties, an alternate synthesis, with improved yield and without using the extremely toxic phosgene, was investigated as shown on scheme.



Scheme

Benzo-1,3-dioxole **2** was first made from catechol, methylene iodide, and ethanolic sodium ethoxide in 1896[5] and numerous preparations have since been described.[6] In this study compound **2** was prepared in 90% yield by the procedures published by Cornforth.[6b] To a heated solution of methylene chloride (15 m*l*) in dimethyl sulfoxide (75 m*l*), catechol (16.0 g) and sodium hydroxide (12.0 g) were added in four portions. After stirring was continued for further 1.5 h, 40 m*l* of water was added and then water-product azeotrope was collected at 98-100 °C. A total of 16.0 g (90%) of colorless oil was obtained by vacuum distillation of the crude product separated from azeotrope; bp 172-174 °C (lit[6b] 173-175 °C); IR(neat) 1220 and 1040cm^{-1} (Aromatic C-O stretching), 735 (1,2-disubstituted benzene); ^{1}H-NMR (CCl_4) δ 6.77(s, 4H, ArH), 5.90ppm(s, 2H, CH_2). 2,2-Dichlorobenzo-1,3-dioxole **3** was prepared in 90% yield by using the similar procedures as described in elsewhere.[7] Compound **2** (15.3g) was treated with fresh PCl_5 (52.4g) in a 13-14g portions. The reaction was vigorous at the addition of first portion of PCl_5, and become sluggish. After standing an hour at room temperature, the reaction mixture was refluxed gently for 2h, then freed from volatile by-products by distillation under moderate vacuum. A total of 21.5g (90%) of colorless oil was obtained by vacuum distillation at 100-105 °C/5 mmHg; IR (neat) 1230 and 1040 cm^{-1} (aromatic C-O stretching), 740 (1,2-disubstituted benzene); ^{1}H-NMR (CCl_4) δ 7.07ppm (s, 4H, ArH). 2,3,7,8-Dibenzo-1,4,6,9-tetraoxaspiro[4,4]nonadiene **4** was synthesized in 81% yield by the similar method published by Gross.[8] 19.3g of **3** in 100 m*l* of dried THF was treated with 12.5 g of catechol. The mixture was warmed at 40 °C for 1.5h to expell HCl. The oily residue obtained by evaporation of THF was triturated with cold ethanol to obtain colorless needles. A recrystallization from ethanol gave 18.7g (81%) of the spiro compound **4** as colorless needles; mp 110-112 °C (lit[8] 109-110 °C); IR(KBr) 1230 and 1170 cm^{-1}(aromatic C-O stretching), 750 (1,2-disubstituted benzene); ^{1}H-NMR ($CDCl_3$) δ6.97ppm (s, 8H, ArH). The overall yield of our alternated synthesis was 66%. Not only the toxic phosgene was not employed in the synthesis but also the yield was improved by 20%.

The polymerization of monomer **4** was carried out by bulk method using BF_3. etherate as catalyst. Monomer **4** (1.00g) purified by sublimation was heated at 115 °C for 60h in a sealed polymerization tube. 0.86g (86%) of pale yellow colored powder was obtained from a reprecipitation from methylene chloride/methanol; [η] 0.04 (0.5g/d*l* $CHCl_3$, 25 °C); IR(KBr) 1750cm^{-1} (C=O stretching); ^{1}H-NMR ($CDCl_3$) δ 7.00ppm (br. s., 8H, ArH). The densities of polymer **5** and monomer **4** were measured at 25 °C to determine the volume change on polymerization by using dilatometer as described on

elsewhere.[3] It was found that monomer **4** was polymerized with 3.8% volume expansion. Bailey[4] also reported that the monomer **4** was polymerized to give a polycarbonate with 3-4 % expansion.

Acknowledgement. This work was supported by the Ministry of Education as a Free Research Project in 1986.

References

1. W. J. Bailey, R. L. Sun, H. Katsuki, T. Endo, H. Iwama, R. Tsushima, K. Saigo and M. M. Bitritto, *J. Polym. Sci., Symposium,* **No 59,** 38 (1977).
2. V. P. Thompson, E. F. Williams and W. J. Bailey, *J. Dent. Res.*, **58,** 1522 (1979).
3. K. H. No, Y. H. Kim and D. K. Kim, *J. Korean Chem. Soc.*, **31,** 98 (1987).
4. W. J. Bailey, M. J. Amone, R. Issari, Y. N. Lin, K. H. No, C. Y. Pan, K. Saigo, J. Stansbury, S. R. Tan, C. Wu, N. Yamazaki and J. Zhou, *Preprint Polym. Mat. Sci. Eng.*, **54,** 23 (1986).
5. C. Moureu, *Bull. Soc. Chim. France,* **15,** 655 (1986).
6. (a) K. N. Campbell, P. F. Hopper and B. K. Campbell, *J. Org. Chem.*, **16,** 1736 (1971); (b) W. Bonthrone and J. W. Cornforth, *J. Chem. Soc.* [*C*] 1202 (1969); (c) H. Fujita and M. Yamashita, *Bull. Chem. Soc. Japan,* **46,** 355 (1973), (d) A. P. Clark, H. L. Holland and J. M. Miller, *Tetrahedron Lett.*, 3361 (1976), (e) A. P. Bashall and J. P. Collins, *ibid,* 3489 (1975).
7. (a) J. S. Buck and F. J. Zimmerman, *Org. Synth.*, **2,** 549 (1943); (b) R. C. Bick and R. A. Russell, *Aust. J. Chem.*, **22,** 1563 (1969).
8. H. Gross, A. Rieche and E. Höft, *Chem. Ber.*, **94,** 544 (1961).

A New Heterocyclic Prostaglandin Analog (I)

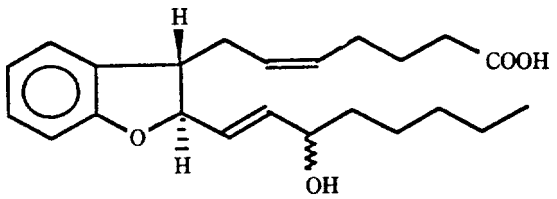
Sung-Eun Yoo*, Kyu Yang Yi

Korea Research Institute of Chemical Technology, Dae Jeon 302-343. *Received November 30, 1988*

Prostaglandin is an important class of compounds in medicinal chemistry possessing wide variety of biological activities, and due to their interesting structural features they have received constant attentions from synthetic organic chemists. They exhibit wide range of biological activities such as gastric acid secretion, cytoprotective action, platelet aggregation, muscle contraction, and blood pressure regulation etc.[1]

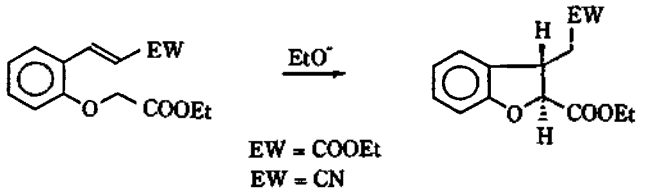
However naturally occurring prostaglandins are, in general, unstable chemically and metabolically. Therefore, over the years, numerous synthetic prostaglandins, called "prostanoids", which are, in general, stable to chemical and biological degradation while retaining biological activities, have been synthesized and evaluated biologically.

In our laboratory, we have been searching for the synthetic prostanoids which satisfy the above requirements. Herein we would like to report a synthesis of a new prostaglandin analog **1** containing a dihydrobenzofuran ring, especially for the thromboxane synthetase inhibitory activity.



1

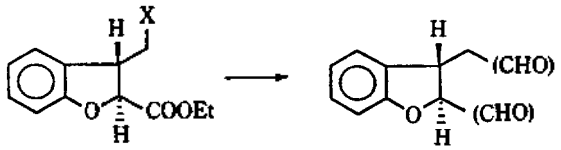
Previously, we have reported an efficient synthesis of a series of 2,3-disubstituted benzofuran derivatives by the intramolecular Michael reaction as depicted in scheme 1.[2] The trans stereochemistry and proper functionality at the 2,3 positions in the molecule make these compounds ideal for the construction of the target molecule, **1**.



EW = COOEt
EW = CN

Scheme 1

The conversion of these compounds to the target molecule **1** requires two consecutive Wittig reactions for the upper and lower side chains. In order to accomplish this task, it is necessary to transform the current functionality on both side chains into the aldehyde functionality stepwise.



X = COOEt **2**
X = CN **5**

Initially we focused our attention on the selective reduction of two ester groups on compound **2**. The DIBAL-H reduction of **2** at −78 °C gave a mixture of **3** and **4**. Other reduction conditions we tried also failed to provide the selective reduction to give **3**. Furthermore attempts on the selective oxidation of two hydroxy groups on **4** which was prepared by the DIBAL-H reduction of **2** at room temperature also gave a mixture of products including the desired product **3**.