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.

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A New Heterocyclic Prostaglandin Analog (I)

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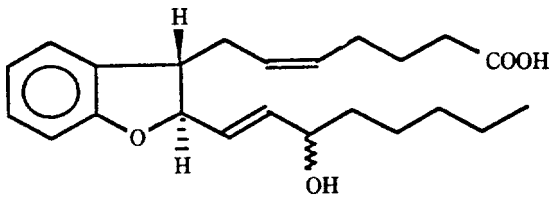
Prostaglandin is an important class of compounds in medicinal chemistry possessing wide variety of biological activities, and due to their interesting structural features they have received constant attentions from synthetic organic chemists. They exhibit wide range of biological activities such as gastric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

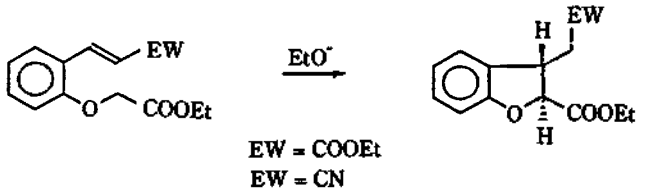
However naturally occurring prostaglandins are, in general, unstable chemically and metabolically. Therefore, over the years, numerous synthetic prostaglandins, called "prostanoids", which are, in general, stable to chemical and biological degradation while retaining biological activities, have been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

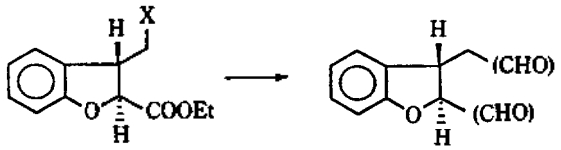
Previously, we have reported an efficient synthesis of a series of 2,3-disubstituted benzofuran derivatives by the intramolecular Michael reaction as depicted in scheme 1.[2] The trans stereochemistry and proper functionality at the 2,3 positions in the molecule make these compounds ideal for the construction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



EW = COOEt
EW = CN

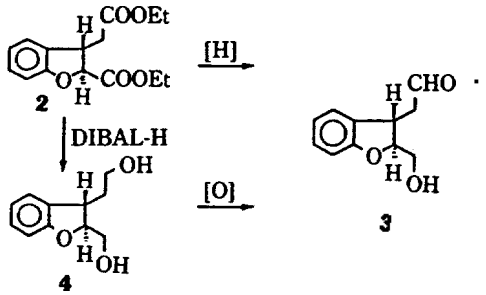
Scheme 1

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.

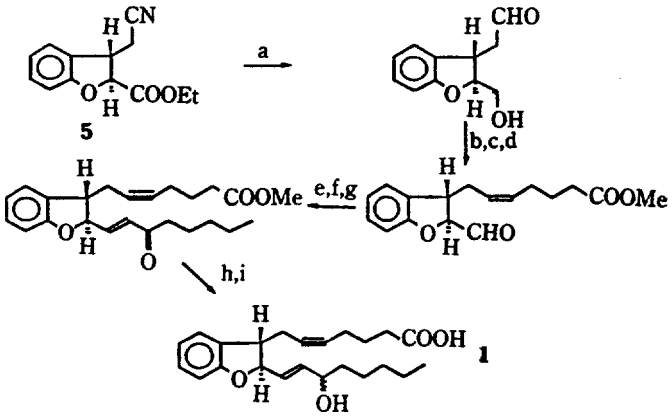


X = COOEt **2**
X = CN **5**

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**.



Scheme 2



a. DIBAL-H, THF, 0°-rt, 2 hrs, and then 5% H_2SO_4, 82%. b. t-Bu $(Me)_2SiCl$, imidazole, DMF, rt, 16 hrs, 95%. c. $P(Ph)_3{}^+(CH_2)_4$ COOH Br^-, t-BuO^-K^+, THF, rt, 4 hrs, 73%[4]. d. CH_2N_2, Et_2O, 0 °C, 0.5 hrs, 100%. e. $(n\text{-}Bu)_4NF$, THF, rt, 1 hr, 87%. f. DMSO, $(COCl)_2$, -50 °C, 1 hr, Et_3N, rt, 1 hr, 72%. g. $(EtO)P(=O)CH_2CO(CH_2)_4CH_3$, LiCl, $(i\text{-}Pr)_2NEt$, CH_3CN, rt, 1 hr, 90%[5]. h. $Zn(BH_4)_2$, Et_2O, 0 °C, 3 hrs, 85% i. NaOH, MeOH, rt, 8 hrs, 95%.

Scheme 3

Therefore, we turned our attention to the cyanoester derivative, **5**, which was also obtained efficiently by the intramolecular Michael reaction described earlier. The DIBAL-H reduction followed by the acidic workup of the cyanoester **5** provided the desired aldehyde-alcohol **3** in high yield. The conversion of **3** to the target molecule **1** proceeded uneventfully as described in scheme 3 and the desired compound **1** was obtained as a thick oil.[3]

Acknowledgement. Financial support for this work by the Ministry of Science and Technology is gratefully appreciated.

References and Footnotes

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   NMR ($CDCl_3$, 270MHz).
   0.88(t, 3H, J = 6.4), 1.29(m, 6H), 1.54(m, 2H), 1.68(m, 2H), 2.09(t, 2H, J = 6.3), 2.33(t, 2H, J = 6.0), 2.45(m, 2H), 3.24(distorted quartet, 1H, J = 6.9), 4.17(m, 1H), 4.74(m, 1H), 5.50(m, 2H).
   IR (neat) 1,713 cm^{-1}.
   Mass (CI-CH4) 373.2 $(M + H)^+$, 257.1, 245.1, 127.0
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Palladium(O) Complex Catalyzed Mono-Carbonylation of Xylylene Dihalides under Phase Transfer Agent(II)

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Phase transfer catalysis is a widely used method in synthetic organic chemistry.[1-3] Recent publications indicate the considerable potential of phase transfer catalysis in effecting metal induced reaction under exceedingly mild condition.[4] Of particular notes are the carbonylation catalyzed by palladium (0) compounds which occurs with high selectivity.[5-6]

In spite of extensive investigations of palladium(0) complex-catalyzed carbonylation of organic halides for the syntheses of esters, amides, aldehydes, and ketones,[7] little attention, however, has been paid to the normal carbonylation of xylylene dihalides.[8]

We reported recently the carbonylation of xylylene dihalides(X = Cl, Br) by using the method of organometallic phase transfer catalysis under an atmospheric pressure of carbon monoxide at room temperature or below.[9] In the course of the study, we found that the carbonylation of xylylene dihalides gave the selectively mono-carbonylated products, (halomethyl)phenylacetic acids.

Various xylylene dihalides could react with carbon monoxide in the presence of dibenzo-18-crown-6-ether or 18-crown-6-ether as a phase transfer agent and palladium(0) complex to afford the corresponding (halomethyl)phenylacetic acid in good yields and phenylenediacetic acid in trace amount under this two-phase system, KOH(aq)/CH_2Cl_2 or