

SHORT  
COMMUNICATIONS

## Unusual Fragmentation of the Enedione Precursor of Thromboxans under Conditions of Hydride Reduction\*

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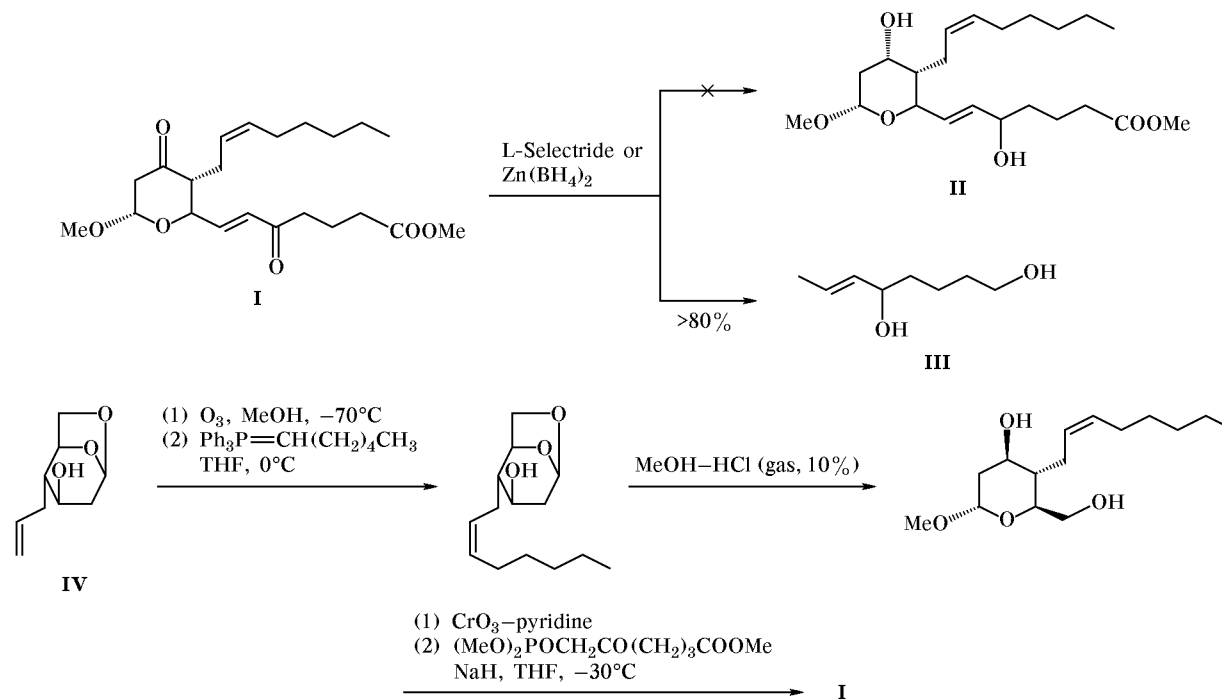
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While accomplishing the total synthesis of 9-LO-thromboxan B<sub>2</sub> (9-LO-TxB<sub>2</sub>) [1, 2] from levoglucosan, at the stage of reduction of enedione **I** with L-Selectride we isolated diol **III** instead of the expected ester 9-LO-TxB<sub>2</sub> (**II**). The reduction under milder conditions [with Zn(BH<sub>4</sub>)<sub>2</sub>] also gave compound **III** (Scheme 1). In both cases we detected no fragmentation products of **I**, containing the missing “upper”

alkene chain and pyran ring. Presumably, these fragments are rapidly involved in further transformations, e.g., oligomerization which is favored by their dicarbonyl nature. The observed fragmentation of **I** under conditions of hydride reduction deserves attention primarily from the viewpoint of its mechanism. Enedione **I** was synthesized from the known levoglucosan derivative **IV** [3] (Scheme 1).

Scheme 1.



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**(+)-6 $\alpha$ -Methoxy-2 $\beta$ -[(1*E*)-6-methoxycarbonyl-3-oxo-1-hexenyl]-3 $\alpha$ -[(2*Z*)-2-octenyl]pyran-3-on (I).**

Oily substance,  $[\alpha]_D^{20} = +6.5^\circ$  ( $c = 0.4$ ,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 0.88 t (3H,  $\text{CH}_3$ ,  $J = 6.9$  Hz), 1.20–1.40 m (6H), 1.90–2.00 m (4H), 2.40 m (4H), 2.70 (5H), 3.33 s (3H,  $\text{OCH}_3$ ), 3.68 s (3H,  $\text{OCH}_3$ ), 4.40 d.d (1H, 2-H,  $J = 6.0, 9.7$  Hz), 5.15 d (1H, 3-H,  $J = 4.0$  Hz), 5.25–5.50 m (2H, *cis*-CH=CH), 6.40 d (1H, *trans*-CH=CH,  $J = 15.8$  Hz) and 6.85 d.d (1H, *trans*-CH=CH,  $J = 6.0, 15.8$  Hz).  $^{13}\text{C}$  NMR spectrum,  $\delta_C$ , ppm: 14.50 ( $\text{CH}_3$ ); 19.91, 22.84, 23.03, 27.90, 29.60, 32.02, 33.52, 40.02, 47.07 ( $\text{CH}_2$ ); 52.02 ( $\text{C}^3$ ); 55.18 (OMe); 55.56 (OMe); 72.25 ( $\text{C}^2$ ); 100.40 ( $\text{C}^6$ ); 126.32, 130.84, 132.51, 142.48 (2CH=CH); 173.90 ( $\text{CO}_2$ ); 199.43, 204.12 (CO).

**( $\pm$ )-6-Octene-1,5-diol (III).**  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.20–1.60 m (6H,  $\text{CH}_2$ ), 1.67 d (3H,  $\text{CH}_3$ ,  $J = 6.7$  Hz), 2.20 br.s (2H, OH), 3.60 t (2H,  $\text{CH}_2\text{O}$ ,  $J =$

6.2 Hz), 4.05 m (1H, CHO), 5.45 d.d (1H, 7-H,  $J = 15.2, 6.1$  Hz), 5.63 m (1H, 6-H).  $^{13}\text{C}$  NMR spectrum,  $\delta_C$ , ppm: 17.67 ( $\text{CH}_3$ ), 21.54 ( $\text{C}^3$ ), 32.34 ( $\text{C}^2$ ), 36.68 ( $\text{C}^4$ ), 62.50 ( $\text{C}^1$ ), 72.92 ( $\text{C}^5$ ), 126.85 ( $\text{C}^7$ ), 132.07 ( $\text{C}^6$ ).

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AM-300 spectrometer in  $\text{CDCl}_3$ .

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