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NOVEL SYNTHESES OF MALTOL AND RELATED COMPOUNDS.

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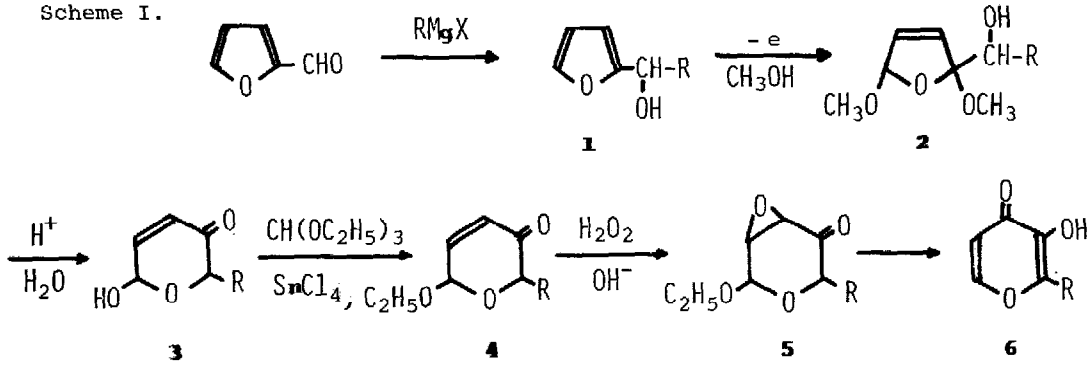
Maltol (2-methyl-3-hydroxy-4H-pyran-4-one) and its related compounds have attracted much attentions because of their remarkable usefulness as a flavoring agent, and much efforts have been made to establish their practical total syntheses,[1] though the partial synthesis from kojic acid is the only hitherto known practical method.[2]

We wish to report here a facile and useful synthetic method in which the starting materials are readily available, the yields are reasonable and the reaction condition is remarkably mild. The reaction pathway is shown in the scheme I.

Scheme I.



The starting 2-(α-hydroxyalkyl)-furan (**1**) was anodically methoxylated to the compound **2** according to the known method.[3] Into an aqueous solution (water, 220ml) of **2** (1.26mole) was added Dowex 50 ion exchange resin (50g) and the solution was stirred at room temperature for ninety minutes. After the resin was filtered off, the filtrate was extracted with ether and the ethereal layer was dried in a refrigerator. Removal of ether under reduced pressure gave **3** as a crystallized solid. The etherification of **3** was accomplished as follows. A solution of dry tetrahydrofuran (60ml) containing **3** (0.0436mole) and ethyl orthoformate (0.131mole) was cooled at -20° and anhydrous tin chloride (1.2g) was added dropwise to the solution. After the addition, the solution was allowed to

stand for half an hour and then it was neutralized by addition of triethylamine. The precipitate was filtered off and the filtrate was dried and distilled to give **4**.

The preparation of epoxy ketone **5** was carried out by the treatment of methanolic solution (80ml) of **4** (0.053mole) and hydrogen peroxide (30%aq, 6.5ml) with sodium hydroxide solution (NaOH 0.2g, water 20ml) at -20°C for one hour.

Epoxy ketone **5** was refluxed in water with Dowex 50 ion exchange resin for 50hr to yield **6**, which were identified by the comparison of spectroscopic and physical data with those of authentic samples. Isolated yields of the products are shown in Table I.

Table I. Isolated Yields of **1** - **6**

R	**1**	**2**	**3**	**4**	**5**	**6**
H	-[a]	61	60	37	26	57
CH_3	83	74	81	66	66	73
C_2H_5	88	73	100	68[b]	48.2[b]	33.4

a) Commercially available
b) Methoxy compound

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