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A Novel Oxidative Ring-Opening of Furans in a $(Br)^+$-Mediated Electrolysis

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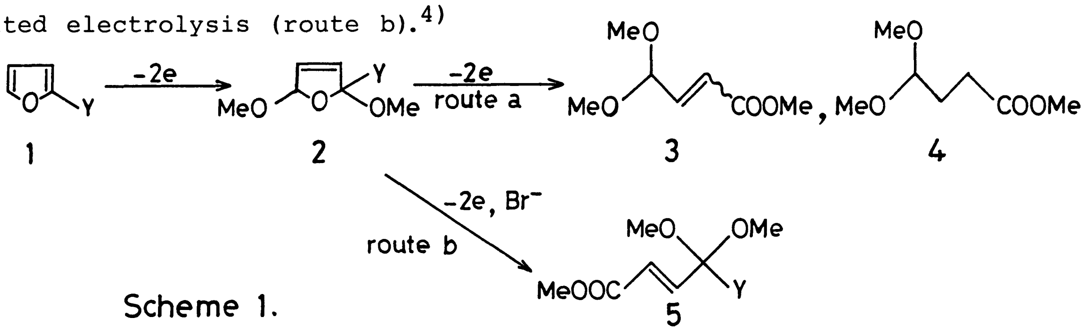
A novel oxidative ring-opening of 2-substituted furans into methyl 4-substituted (E)-4,4-dimethoxy-2-butenoates has been performed by electrolysis in an NH_4Br-Et_4NClO_4-MeOH-(Pt electrodes) system.

Direct transformation of furans into the open-chain 1,4-dicarbonyl synthons is of importance for a facile access of useful synthetic blocks.[1] We and Iwasaki et al. have reported the electrolytic ring-opening of 2-substituted furans **1** (Y = COOH, CHO, CH_2OH, etc.) into methyl (E)- and (Z)-4,4-dimethoxy-2-butenoates **3**[2] and methyl 4,4-dimethoxybutanoate **4**.[3] The transformation involves a two-electron oxidation of **1** into the corresponding 2,5-dimethoxy-2,5-dihydrofurans **2** followed by the electro-oxidative fission of the C(2)-substituents to give **3** and **4** (route a). We wish to report a novel oxidative ring-opening of 2-substituted furans **1**, which can be achieved without loosing C(2)-substituents (Y), by a $(Br)^+$-mediated electrolysis (route b).[4]



Scheme 1.

The electrolysis was carried out in an undivided cell fitted with two Pt electrodes (1.5 x 2 cm^2). A typical procedure is as follows. A mixture of methyl 2-furoate **1a** (Y = $COOCH_3$, 2 mmol), NH_4Br (20 mg), Et_4NClO_4 (100 mg) in MeOH (7 ml) was electrolyzed under a constant current (100 mA/cm^2) at an ambient temperature. After passage of 13 F/mol of electricity, workup of the electrolytes afforded **5** (Y = $COOCH_3$, 85%).

The presence of NH_4Br in the electrolysis media is indispensable, since absence of NH_4Br resulted in >90% recovery of the intermediary **2a** (Y = COOMe) even after passage of 15 F/mol of electricity. The yield of **5a** is affected by Br^-

Table 1. Electrolytic Ring-Opening of Furans

Entry	Substrate		Electricity	Yield of 5
	Y		F/mol	%
1	**1a**	COOMe	15	85
2[a)]	**1b**	CH_2OAc	10	84
3	**1c**	CH_2OH	15	70
4	**1d**	CHO	15	78[b)]
5	**1e**	CH_3	10	67

a) $MgSO_4$ (100 mg) was added to prevent methanolysis of the acetate moiety.

b) Y = $CH(OMe)_2$.

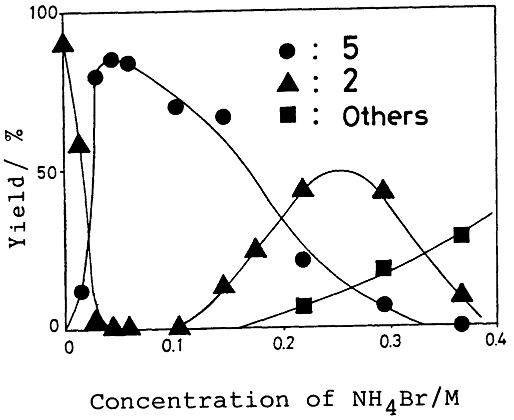


Fig. 1. Isolated yields after passage of 13 F/mol of electricity (100 mA/cm^2).

concentration in the electrolysis media (Fig. 1). Thus, at lower Br^- concentration (0.03-0.1 M), the ring-opening reaction takes place to give **5**, while at higher Br^- concentration (> 0.2 M), the generation of Br_2 predominates⁵⁾ and gives **2a** as a major product.⁶⁾

In Table 1 are listed examples of the ring-opening reaction of various 2-substituted furans **1** and isolated yields of **5**. Alcohol **1c** and aldehyde **1d** were converted to the corresponding ring-opened products **5c** and **5d** (Y = $CH(OMe)_2$) without any detectable amounts of **3** and **4**.²⁾ Although the details of the reaction mechanism have not been clarified yet, it is very likely that electrogenerated $(Br)^+$, e.g., Br^+, Br_3^+, and BrOMe, plays an important role in the ring-opening reaction.

References

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2) H. Tanaka, Y. Kobayashi, and S. Torii, J. Org. Chem., 41, 3482 (1976); O. Kawana, Y. Nakamura, and Y. Yoshihiro, Nippon Kagaku Kaishi, 1983,1747.

3) T. Iwasaki, T. Nishitani, H. Horikawa, and I. Inoue, J. Org. Chem., 47, 3799 (1982).

4) A similar ring-opening reaction of 2-methoxycarbonylthiophene into **5a** (52% yield; E/Z mixture) has been reported: M. Janda, J. Srogl, M. Nemec, and A. Janousova, Collect. Czech. Chem. Commun., 38, 1221 (1973).

5) C. Vanleugenhaghe, G. Valensi, H. Pourbaix, "Atlas of Electrochemical Equilibrium in Aqueous Solutions," ed by M. Pourbaix, Pergamon Press, Oxford (1966), p. 640.

6) Reaction of **2a** with Br_2 in MeOH afforded no appreciable amount of **5**.

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