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The Synthesis of 5,5′-Di-(2-methoxycarbonyl-vinyl)-2,2′-bifuryl by the Electrolysis of Methyl 3-(2-Furyl)acrylate[1]

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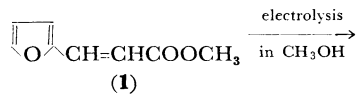
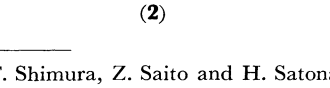
The present authors previously reported the synthesis of methyl 3-(2,5-dimethoxy-2,5-dihydrofuryl)acrylate (**2**) by the electrolysis of methyl 3-(2-furyl)acrylate (**1**) and the decomposition of **2**.[2-5]



(**1**)



(**2**)

1) Paper 5 on "The Synthesis of Unsaturated Carboxylic Acid by the Ring-opening Reaction of Furan Compounds."

2) T. Shimura and Z. Saito, *Nippon Kagaku Zasshi*, **89**, 695 (1968).

3) T. Shimura, Z. Saito, M. Koizumi and H. Satonaka, *ibid.*, **90**, 96 (1969).

4) T. Shimura, Z. Saito and H. Satonaka, *ibid.*, **90**, 716 (1969).

5) T. Shimura, Z. Saito and H. Satonaka, *ibid.*, **90**, 1173 (1969).

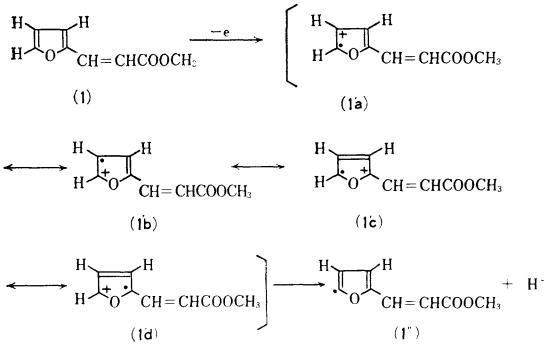
This paper will describe a new compound formed by the electrolysis of methyl 3-(2-furyl)acrylate (**1**) in methyl alcohol at low temperatures (−40—−50°C). When the electrolysis was carried out by use of the Clauson-Kaas method,[6] methyl 3-(2,5-dimethoxy-2,5-dihydrofuryl)acrylate (**2**) was mainly formed, a yellow precipitate was also obtained.

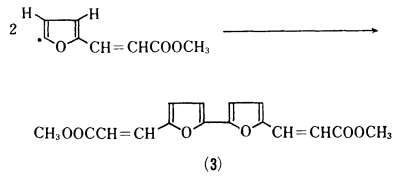
The IR spectrum of the yellow product showed an unsaturated ester carbonyl band at 1721 cm^{-1}, an olefinic band at 1638 cm^{-1}, and bands of the furan ring at 1023 and 881 cm^{-1}. The UV spectrum in methyl alcohol showed a maximum peak with a molecular extinction coefficient of 46000 at 392 mμ and a shoulder band at 410 mμ.

The NMR spectrum showed signals at τ 2.59 (2H, doublet, J=15 Hz), 3.27 (2H, doublet, J=5 Hz), 3.35 (2H, doublet, J=5 Hz), 3.62 (2H, doublet, J=15 Hz), and 6.21 (6H, singlet). The signals at τ 2.59 and 3.62 with the spin-spin coupling constant of 15 Hz were assigned to the methin protons of –CH=CH– in the acrylate group. The doublets at 3.27 and 3.35 with the J of 5 Hz were assigned to the protons of the furan ring. The signal at τ 6.21 was assigned to the methyl protons of the methyl ester. The elementary analysis data agreed with the formula of $C_{16}H_{14}O_6$.

On the basis of these results, the product was determined to be a dimer of methyl 3-(2-furyl)-acrylate, 5,5′-di(2-methoxycarbonyl-vinyl)-2,2′-bifuryl (**3**).

This dimer seems to be formed at the anode. The reactions may proceed as follows:





The anodic oxidation of furylacrylate (**1**) may give a radical cation which can be expressed in terms of the resonance hybrid of the four structures, **1′a**, **1′b**, **1′c**, and **1′d**, and this radical cation may then turn into a radical **1″** and a proton. At last, the coupling reaction of **1″** takes place to give **3**. The bifuryl thus formed seems to be deposited from the reaction mixture because of its small solubility.

This dimer is an interesting material which belongs to an unsaturated dibasic carboxylic acid and which contains two furan rings.

Experimental

Methyl 3-(2-Furyl)acrylate (1). This material was prepared by the condensation of furfural with methyl acetate by the method of Gilman *et al.*[7] Yellow crystals; mp 27°C.

5,5′-Di(2-methoxycarbonyl-vinyl)-2,2′-bifuryl (3). To a solution of 20 g of methyl 3-(2-furyl)acrylate in 250 m*l* of methyl alcohol, 1 m*l* of concentrated sulfuric acid was added; the mixture was then electrolyzed in a Clauson-Kaas electrolyser[6] for 6 hr with 10—12 V, 1.5 A at −40——50°C. A yellow product was obtained by the subsequent filtration of the electrolyzed solution. Recrystallization from methyl alcohol gave yellow needles with a melting point of 184°C; 2 g (10%).

Found: C, 63.40; H, 4.77%. Calcd for $C_{16}H_{14}O_6$: C, 63.57; H, 4.67%.

IR (cm^{-1}, KBr): 3130($\nu_{=C-H}$), 1721($\nu_{C=O}$), 1638 ($\nu_{C=C}$), 1023, 881(furan nucleus).

UV(λ_{max} mμ(ε), in CH_3OH): 392 (46000), 410 (39000), 228 (22000), 289 (9000).

NMR (τ, in $CDCl_3$): 6.21 (6H, s), 3.62 (2H, d, J=15 Hz), 2.59 (2H, d, J=15 Hz), 3.35 (2H, d, J=5 Hz), 3.27 (2H, d, J=5 Hz).

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6) N. Clauson-Kaas and F. Linborg, *Acta Chem. Scand.*, **6**, 531 (1952).

7) H. Gilman and R. E. Brown, *Iowa State College J. Sci.*, **2**, 317; *Chem. Abst.*, **22**, 4524 (1928).