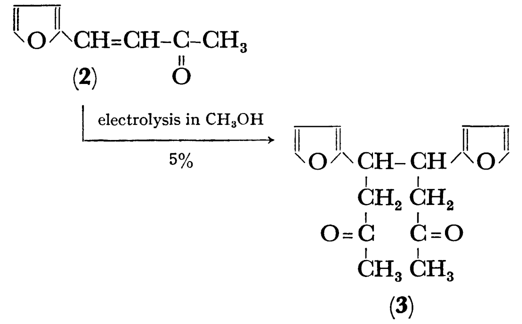
BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2892—2893 (1973)

The Synthesis of (4,5-Di(2-furyl)-2,7-octanedione) by the Electrolysis of (4-(2-Furyl)-3-buten-2-one)

Hajime SATONAKA, Zei SAITO, and Toshio SHIMURA
Industrial Research Institute of Kanagawa Prefecture, Showa-machi, Kanazawa-ku, Yokohama 236

(Received December 1, 1972)

4-(2-Furyl)-3-buten-2-one (**2**), which resembles methyl 3-(2-furyl)acrylate (**1**), was electrolyzed in methyl alcohol containing sulfuric acid as a supporting electrolyte. While **1** was oxidized to methyl 3-(2,5-dimethoxy-2,5-dihydrofuryl)acrylate[1-4] and 5,5′-bis[2-(methoxycarbonyl)vinyl]-2,2′-bifuryl,[5] **2** was reduced to 4,5-di(2-furyl)-2,7-octanedione (**3**) under similar conditions.



The IR spectrum of the dimer (**3**) showed a carbonyl band at 1708 cm^{-1} and bands of the furan ring at 3125, 1511, 1020, 886, and 758 cm^{-1}.[6] The UV spectrum in methyl alcohol showed a maximum peak at 220 mμ with a molar extinction coefficient of 11000. The NMR spectrum showed signals of furan-ring protons at τ 2.68 (2H, multiplet), 3.78 (2H, multiplet), and 3.91 (2H, multiplet), of methin protons at 6.40 (2H, multiplet), of methylene protons at 7.35 (4H, multiplet), and of methyl protons at 8.07 (6H, singlet). The mass spectrum exhibited its intense peaks

---

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

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

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

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

[5] H. Satonaka, Z. Saito, and T. Shimura, This Bulletin, **43**, 2633 (1970).

[6] M. Yamaguchi, *Bunsekikagaku*, **7**, 210 (1958).

at m/e 274 (M^+), 217 ($M^+-CH_2COCH_3$), 137 ($M^+/2$), and 43 ($^+COCH_3$). The elementary analysis agreed with the formula of $C_{16}H_{18}O_4$. On the basis of these results, the product was determined to be 4,5-di(2-furyl)-2,7-octanedione (**3**).

Table 1. Yields of 4,5-difuryl-2,7-octadione by the electrolyses in the various solvents (%)[a]

Solvent	Yield	Solvent	Yield
CH_3OH	5	DMF	5
C_2H_5OH	2	Pyridine	3
$(CH_3)_2CO$	7	Dioxane	Trace
THF	1		

a) Averages of the three times experiments.

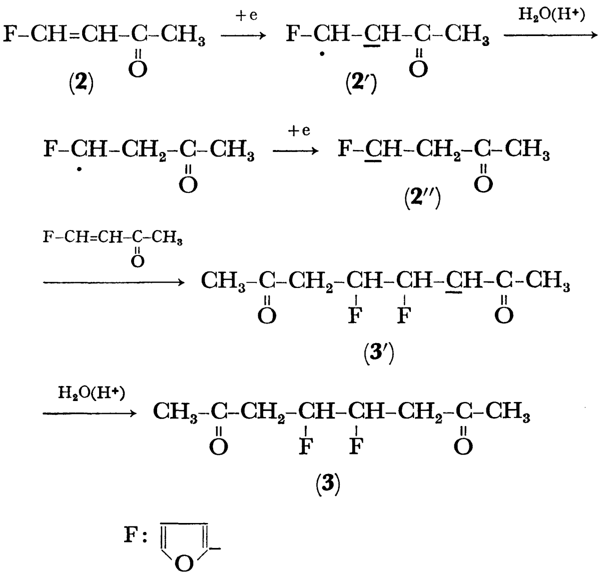
Similar electrolyses were repeated for ethyl alcohol, acetone, tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), pyridine, and dioxane in the same way as was used for in methyl alcohol. The yields of the product are given in Table 1. The results when water was mixed in methyl alcohol, acetone, and DMF in various proportions, and when the reactions were carried out in these mixed solvents, are given in Table 2. It was found that the yields increased with the addition of water and came to a maximum at the point where the volume of water amounted to about 50—70%.

Table 2. Yields of 4,5-difuryl-2,7-octadione in the various water-mixed solvents (%)[a]

Solvent	H_2O (%)			
	10	25	35	50
CH_3OH	6	24	15	4
$(CH_3)_2CO$	45	52	46	34
DMF	24	30	40	15

a) Average of the three times experiments

Assuming that these reactions proceed by means of a mechanism similar to that in the hydrodimerization of acrylonitrile,[7-11] furfurylideneacetone (**2**) can be said to undergo an over-all two-electron uptake at the cathode. This probably occurs in two one-electron stages. The radical anion (**2′**) may react with water (or the proton) before the second electron is taken up. The carbanion (**2″**) may attack highly-polarized molecules of the monomer attracted to the cathode. The interaction of the dione anion (**3′**) with water (or the proton) might terminate the reactions and yield 4,5-di(2-furyl)-2,7-octanedione (**3**).



$$\underset{(2)}{\text{F-CH=CH-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-CH}_3} \xrightarrow{+e} \underset{(2')}{\text{F-}\underset{\bullet}{\text{CH}}\text{-}\underline{\text{C}}\text{H-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-CH}_3} \xrightarrow{H_2O(H^+)}$$

$$\text{F-}\underset{\bullet}{\text{CH}}\text{-CH}_2\text{-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-CH}_3 \xrightarrow{+e} \underset{(2'')}{\text{F-}\underline{\text{C}}\text{H-CH}_2\text{-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-CH}_3}$$

$$\xrightarrow{\text{F-CH=CH-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-CH}_3} \underset{(3')}{\text{CH}_3\text{-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-CH}_2\text{-}\underset{\underset{\text{F}}{|}}{\text{CH}}\text{-}\underset{\underset{\text{F}}{|}}{\text{CH}}\text{-}\underline{\text{C}}\text{H-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-CH}_3}$$

$$\xrightarrow{H_2O(H^+)} \underset{(3)}{\text{CH}_3\text{-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-CH}_2\text{-}\underset{\underset{\text{F}}{|}}{\text{CH}}\text{-}\underset{\underset{\text{F}}{|}}{\text{CH}}\text{-CH}_2\text{-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-CH}_3}$$

Experimental

4-(2-Furyl)-3-buten-2-one (2). This material was prepared by the condensation of furfural with acetone by the method of G. J. Leuck *et al.*[12] Yellow crystals; mp 37—39 °C.

4,5-Di(2-furyl)-2,7-octanedione (3). To a solution of 10 g of 4-(2-furyl)-3-buten-2-one in 200 ml of methyl alcohol, 1 ml of conc. sulfuric acid was added; the mixture was then electrolysed in a Clauson-Kaas electrolyser[13] for 4 hr with 15 V, 1—2 A at −40—−50 °C. A product was obtained by the subsequent filtration of the electrolyzed solution. Recrystallization from methyl alcohol gave colorless needles with a melting point of 123 °C; 0.5 g (5%). The experiments using other solvents and the water-mixed solvents were carried out under similar conditions.

Found: C, 70.25; H, 6.51%. Calcd for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61%.

IR (cm^{-1}, KBr): 3125 ($\nu_{=C-H}$), 1708 ($\nu_{-C=O}$), 1511, 1020, 886, 758 (furan nucleus).

UV (λ_{max} mμ(ε), in CH_3OH): 220 (11000).

NMR (τ, in CCl_4): 2.68 (2H, m), 3.78 (2H, m), 3.91 (2H, m) (furan nucleus protons), 6.40 (2H, m, methin protons), 7.35 (4H, m, methylene protons), 8.07 (6H, s, methyl protons).

Mass spectrum: m/e 274 (M^+), 217 ($M^+-CH_2COCH_3$), 137 ($M^+/2$), 43 ($^+COCH_3$).

The authors wish to express their thanks to Dr. Minoru Hirota, Yokohama National University, for his kind suggestions and encouragement, and Mr. Tetsuya Yokokawa and Mr. Takayoshi Ozawa for thier help in the mass-spectrum measurements and elementary analysis.

---

[7] M. M. Baizer, *J. Electrochem. Soc.*, **111**, 215 (1964).

[8] K. Sugino and T. Nakaya, *ibid.*, **112**, 1241 (1965).

[9] Y. Arad, M. Levy, I. R. Miller, and D. Vofsi, *ibid.*, **114**, 899 (1967).

[10] M. Figeys and H. P. Figeys, *Tetrahedron*, **24**, 1097 (1968).

[11] I. Gillet, *Bull. Soc. Chim. Fr.*, **1968**, 1929.

[12] G. J. Leuck and L. Cejka, "Organic Syntheses," Coll. Vol. I, p. 283 (1956).

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