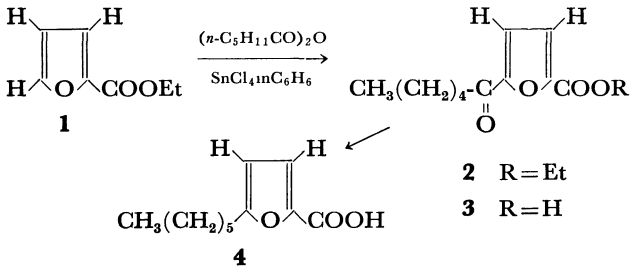
Anodic Reaction of 5-Alkyl-2-furoic Acids in Protic Solvents

Sigeru Torii, Hideo Tanaka, Hitosi Ogo, and Siro Yamasita
Department of Industrial Chemistry, Okayama University, Okayama
(Received August 26, 1970)

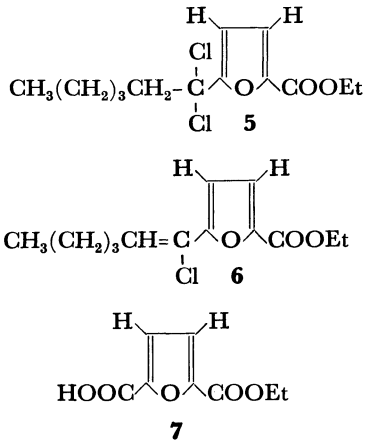
Anodic oxidation of 5-alkyl-2-furoic acids (**4** and **10**) in protic solvents has been studied. The major products were 1-butenolides (**12**, **13**, **16**, and **17**) and γ-keto esters (**11** and **15**) and their acids (**14** and **18**). Methyl 5-*n*-hexyl-2,5-dimethoxy-2,5-dihydro-2-furoate **19** was converted into γ-keto ester **11** and its acid **14** by hydrolysis with alkali and into 1-butenolide **12** by electrolysis of the alkaline solution. A possible mechanism of the anodic oxidation of 5-alkyl-2-furoic acids has been discussed.

Anodic oxidation of a number of furan derivatives in protic media in the presence of appropriate electrolytes gives mainly 2,5-disubstituted 2,5-dihydrofurans.[1] However, similar experiments on 2-furoic acids have not been described, except for one by Hellström.[2] We are especially interested in 2-furoic acids both for their synthetic utility[3,4] and for anodic oxidation that is expected on both the furan ring and carboxyl group. We report that the anodic oxidation of 5-*n*-hexyl and 5-



1 **2** R=Et **3** R=H **4**

(1,1-dimethylbutyl)-2-furoic acids (**4** and **10**) in protic media can lead to γ-hexyl-γ-keto acid derivatives and also to γ-alkyl-1-butenolides, which can be rationalized as arising from 2,5-substituted intermediates (b).



5 **6** **7**

5-Alkyl-2-furoic acids have been synthesized by Gilman and Calloway[5] from the condensation of alkyl 2-furoates with alkyl halides using aluminum chloride. *n*-Alkyl chains are found to be isomerized to give secondary and tertiary derivatives.[5] An attempt to prepare 5-*n*-alkyl-2-furoic acids by the reaction of 2-furoates with acid anhydrides has been reported.[6]

The reaction of ethyl 2-furoate **1** with *n*-hexanoic anhydride in the presence of stannic chloride was reinvestigated and found to give a 4—10% yield of oily materials which seem to be a mixture containing **5** and **6**, in addition to the expected crystalline ester (**2**, 15—20%). A constituent of the crude oil was isolated by preparative vpc after treatment with pyridine, and assigned to be **6** on the basis of spectral data and elemental analysis.

In the initial stage of this reaction, a large amount of *gem*-dichloride **5** is believed to be produced, but the high reactivity and instability of the dichloride function has precluded its isolation and characterization. As a matter of fact, halide **6** was converted into 5-carbethoxy-2-furoic acid[7] liberating hydrogen chloride while the oil stood at room temperature for several hours. Preferential formation of the mixture of chlorides (**5** and **6**) over **2** occurred when the reaction of **1** with *n*-hexanoyl chloride in carbon tetrachloride was carried out using ferric chloride as a catalyst.[8] Conversion of **2** into **4** *via* **3** was realized by the Huang-Minlon reduction.[9]

We studied in detail the structure of the products in the alkylation of **1** with *n*-hexyl bromide. By fractional distillation, two components of bp 140—142.5°C/20 mmHg could be isolated in the ratio 3:1 and the analytical specimens (**8** and **9**) were obtained by preparative vpc. The structure of **8**, a fraction boiling at 142°C/20 mmHg, was assigned from spectral data and elemental analysis. By comparing the NMR spectrum of **8** with that of **9**, a conspicuous difference was found at τ 8.00—9.50. In this region the NMR spectrum of **9** exhibited a triplet at 9.26 (6H), a singlet at 8.78 (3H), a triplet at

1) a) N. L. Weinberg and H. R. Weinberg, *Chem. Revs.*, **68**, 499 (1968); b) S. D. Ross, M. Finkelstein, and J. J. Uebel, *J. Org. Chem.*, **34**, 1018 (1969); c) S. Arita, Y. Takahashi, and K. Takeshita, *Kogyo Kagaku Zasshi*, **72**, 2289 (1969); d) K. Yoshida and T. Fueno, This Bulletin, **42**, 2411 (1969).

2) N. Hellström, *Svensk Kem. Tid.*, **60**, 214 (1948); *Chem. Abstr.*, **43**, 1271 (1949).

3) A. Takeda, H. Hosisima, and S. Torii, This Bulletin, **39**, 1354 (1966).

4) A. Takeda, K. Takahashi, S. Torii, and T. Moriwake, *J. Org. Chem.*, **31**, 616 (1966).

5) Isolation of the corresponding side chain isomers was not attempted: H. Gilman and N. O. Calloway, *J. Amer. Chem. Soc.*, **55**, 4197 (1933).

6) Without isolating intermediates, impure oily 5-alkyl-2-furoic acids were used for the synthesis of antitubercular active compounds: K. Kawabe, T. Suzui, and M. Iguchi, *Yakugaku Zasshi*, **80**, 58 (1960).

7) R. Andrisano and A. Tundo, *Gazz. Chim. Ital.*, **81**, 414 (1951); *Chem. Abstr.*, **46**, 55736 (1952); Beilstein Org. Chem., H. **18**, 329.

8) G. G. Galustyan and I. P. Tsukervanik, *Zh. Obshch. Khim.*, **34**, 1478 (1964).

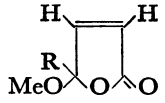
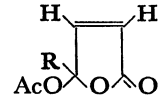
9) Huang-Minlon. *J. Amer. Chem. Soc.*, **68**, 2487 (1964).

Table 1. Reaction procedures and yields of products

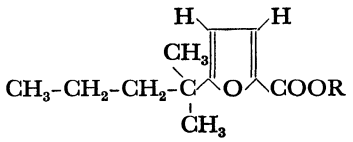
Experiment	1	2	3	4	5	6
Substrate	4	4	4	11	11	11
(g)	1.5	1.0	0.9	2.7	1.8	0.8
Solvent						
AcOH* (ml)	20+60*a)	35+10*b)	—	50+100*c)	20+40*d)	—
MeOH (ml)	15	—	20	10.2	15	20
H_2O (ml)	10	—	10	15.5	10	10
Electrolyte	KOH	AcONa	KOH	KOH	KOH	KOH
(g)	0.65	0.6	0.3	1.15	0.65	0.3
Reaction Time (hr)	26	8	2	24	27	2.5
Terminal Voltage (V)	16—17	50	15	15	15	12
Current (A)	0.8—1.2	0.2—0.3	1.0	1.3—1.8	0.7—1.2	1.0
Temp (°C)	29—34	28—35	25—26	25—35	25—30	19—20
End point (pH)	4	—	8	4	4	8
Procucts						
Neutral (g)	1.2	0.8	0.7	2.0	1.3	0.7
Acidic (g)	0.3	—	0.15	0.5	0.1	0.15

* After electrolysis was continued for 2—3 hr, additional acetic acid was added as follows: a) 10 ml every 4 hr, b) 5 ml every 2.5 hr, c) 10 ml every 2 hr, d) 10 ml every 5 hr.

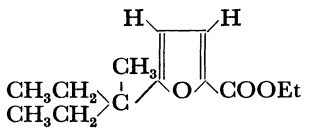
Table 2. Composition of the products (peak area % on vpc)

Experiment	1	2	3	4	5	6
Constituents R	n-C_6H_{13}-			$CH_3(CH_2)_2C(CH_3)_2$-		
Neutral portion						
R-CO-CH_2-CH_2-COOMe	28	—	42	5	26	83
	46	—	21	18	32	(11)[a]
	—	71	—	30	—	—
Unknown	—	—	37	—	—	—
Others (several peaks)	26	29	—	47	42	6
Acidic portion						
R-CO-CH_2-CH_2-COOEt	60	—	93	61	60	97

a) Identification was carried out by comparison of retention time on vpc.



8 R=Et
10 R=H



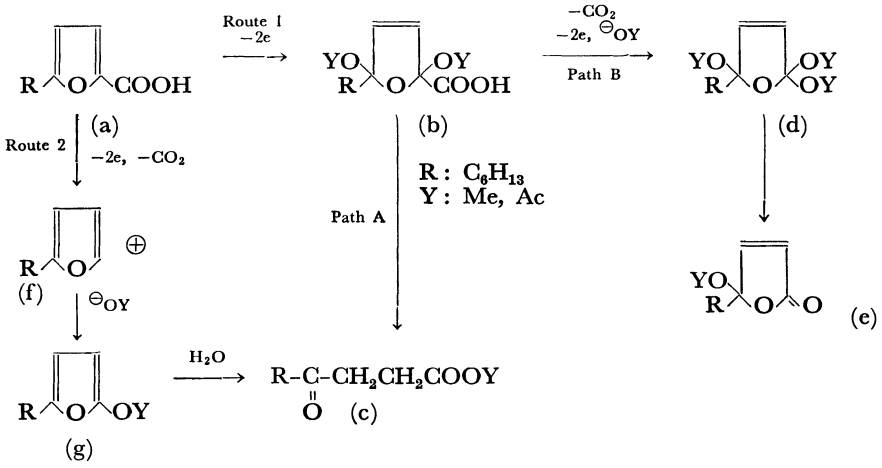
9

8.65 (3H), and a multiplet at 8.34 (4H). Except for the region 1250—1150 cm^{-1} the infrared spectra of **8** and **9** are similar with respect to all major peaks. Hydrolysis of **8** in the usual manner gave **10** in good yield.[5]

Electrolysis of furoic acids (**4** and **10**) was carried out in various protic media, using two platinum foil electrodes. Details of the experimental conditions along with the results are shown in Tables 1 and 2. In runs 1 and 5, mixtures of γ-keto esters (**11** and **15**), 1-butenolides (**12** and **16**) and γ-keto acids (**14** and **18**) were obtained. In experiments 2 and 4, an increase in the proportion of acetic acid in the electrolyte solution facilitated the formation of γ-acetoxy-1-butenolides (**13** and **17**). In procedures 3 and 6, formation of both γ-keto acids (**14** and **18**) and their methyl esters (**11** and **15**) increased considerably. Analytical samples of these compounds were obtained by preparative vpc.

The structures of **11** and **14** were confirmed by comparison of their NMR and infrared spectra with those of authentic specimens.[4,10] The proposed structure for **15** was supported by its infrared spectrum, showing γ-keto ester carbonyls at 1745 and 1709 cm^{-1}, and

10) Authentic methyl 4-oxo-decanoate was prepared from the corresponding acid by methylation with diazomethane.



Scheme 1

11 R=*n*-C_6H_{13}- R'=CH_3
14 R=*n*-C_6H_{13}- R'=H
15 R=$CH_3(CH_2)_2C(CH_3)_2$- R'=CH_3
18 R=$CH_3(CH_2)_2C(CH_3)_2$- R'=H

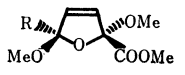
12 R=*n*-C_6H_{13}-
16 R=$CH_3(CH_2)_2C(CH_3)_2$-

13 R=*n*-C_6H_{13}-
17 R=$CH_3(CH_2)_2C(CH_3)_2$-

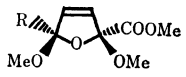
by its NMR spectrum which shows geminal methyls at τ 8.86 as a singlet, and also by its elemental analysis. The γ-keto acid **18** was converted into **15** by the action of diazomethane. The structures of γ-methoxybutenolides (**12** and **16**) were deduced from their spectral properties and elemental analyses. The infrared spectra of both **12** and **16** had equal absorption bands at 3100, 1830, 1778, and 1613 cm^{-1}. NMR spectra of **12** and **16** exhibited a three-proton signal at τ 6.88 and 6.83, respectively, in place of the peak at τ 7.92 due to methyl protons of the acetoxy group of **13** and **17**. The NMR spectrum of **17** showed two doublets at τ 2.56 and 3.71 (J=6Hz) ascribable to olefinic protons. The NMR spectrum of **13** closely resembled that of **17**. Further evidence confirming the structural similarity of **13** and **17** was found in the absorption bands at 1786 and 1760 cm^{-1} due to lactone and acetoxy carbonyls, respectively.

The electrochemical behavior of 5-alkyl-2-furoic acids (a) is of particular interest in clarifying competitive anodic oxidation between the furan ring and carboxyl group. A tentative mechanism for the formation of γ-keto derivatives (c) and 1-butenolides (e) is shown in Scheme 1. As seen in route 1, anodic oxidation of furoic acids (a) would occur *via* two electron oxidation of the furan ring similar to the mechanism previously proposed, which involves cation radical or dication intermediates.[1] On the other hand, plausible intermediates (g) that may be derived from two electron oxidation of the carboxyl group of (a) *via* cation precursor (f) as shown in route 2 might be subjected to hydrolysis to give (c). Some evidence is required of the presence of the obtainable intermediates (g) in the initial products from the anodic oxidation of (a), but no appreciable amount of (g) was detected on vpc. Thus, it seems that an initial oxidation mechanism of the furan ring (route 1) for the anodic oxidation of (a) accounts for the results.

In order to obtain evidence for the proposed mechanism, anodic oxidation of (b) under our conditions was attempted. Anodic oxidation of methyl 5-*n*-hexyl-2-furoate in methanol in the presence of a catalytic amount of sulfuric acid afforded *trans* and *cis* isomers of 2,5-dimethoxy derivatives (**19**a and **19**b). Isolation of both **19**a and **19**b could be carried out by preparative vpc.

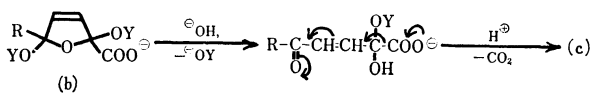


19a, *trans*



19b, *cis*

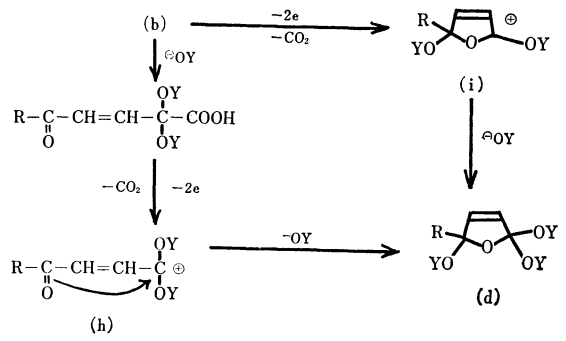
Hydrolysis of **19** in aqueous methanol-potassium hydroxide gave an alkaline solution from which only γ-keto ester **11** and γ-keto acid **14** were obtained after acidification with dilute sulfuric acid. Evolution of carbon dioxide took place when the pH of the alkaline solution fell below 7. This suggests that 2, 5-dimethoxy derivative (b) is a precursor of **11** and **14** (path A). On the other



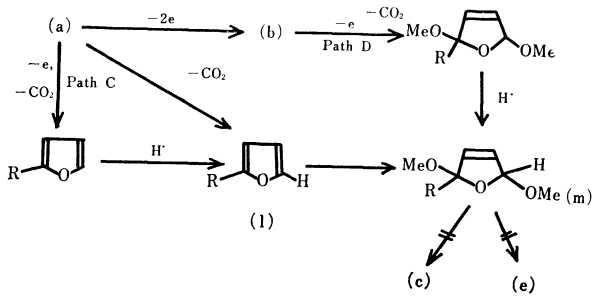
Y=H, Me Path A

hand, electrolysis of the alkaline solution gave 10—15% yield of 1-butenolide **12** together with **11** and **14**. The result reveals the probability of 2,5-dimethoxy derivative (b) as an intermediate which can lead to **12** (path B). Further two electron oxidation of the carboxyl group of (b) might give an unstable compound (d) *via* cation intermediates (h and/or i) as shown in Scheme 2.

Alkaline hydrolysis, followed by treatment with mineral acid, of 2,5-dimethoxy-2-*n*-hexyl-2,5-dihydrofuran (m) resulting from anodic dimethoxylation of 2-*n*-hexylfuran (l), which may be derived from one electron oxidation of (a) and (b) as shown in path C and D in



Scheme 2



Scheme 3

Scheme III, provided no evidence for the presence of (c) and (e).

Experimental[11]

Reaction of Ethyl 2-Furoate (1) with n-*Hexanoic Anhydride.* Condensation of **1** (14.0 g) with *n*-hexanoic anhydride (21.4 g) in benzene (50 ml) in the presence of stannic chloride (52 g) was carried out. A mixed oil was obtained (7.1 g) according to the procedure reported by Kawabe *et al.*[6] Upon standing for several hours, white crystals **2** were precipitated and purified by preparative vpc to give analytical sample of **2**, mp 57—58°C: IR (neat) 3150 (=C–H), 3100 (=C–H), 1730 (ester C=O), 1675 (C=O), 1570 (C=C), 1503, 1295, 1260, 1220, 1165, 1015, 960, 770 cm^{-1}; NMR ($CDCl_3$) τ 2.80 (s, 2H, =C–H), 5.60 (q, 2H, J=5.6 Hz, O–CH_2–C), 7.10 (t, 2H, –CH_2CO), 8.25 (m, 8H, –$(CH_2)_4$–), 8.60 (t, 3H, J=5.6 Hz, O–C–CH_3), 9.10 (t, 3H, C–CH_3).

Found: C, 65.78; H, 7.82%. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61%.

Ketonic component **2** was separated from the oily filtrate by extraction with Girard reagent P.[12] A total 4.5 g of **2** was obtained. The residual yellow oil, after being treated with a few drops of pyridine, was purified by distillation to give 2.2 g of **6**, bp 125—128°C/2 mmHg. The analytical specimen was obtained by preparative vpc; IR (neat) 3150 (=C–H), 3100 (=C–H), 1725 (ester C=O), 1640 (C=C), 1580 (C=C), 1510, 1300, 1258, 1211, 1140, 1014, 800, 755 cm^{-1}; NMR ($CDCl_3$) τ 2.86 (d, 1H, J=2.7 Hz, =C–H), 3.36 (t, 1H, J=5.6 Hz, CCl=C–H), 3.40 (d, 1H, J=2.7 Hz, =C–H), 5.60 (q, 2H, J=5.6 Hz, O–CH_2–C), 7.58 (m, 2H, =C–CH_2), 8.00—8.70 (m, 4H, –$(CH_2)_2$–), 8.60 (t, 3H, J=5.6 Hz, O–C–CH_3), 9.07 (t, 3H, C–CH_3).

Found: C, 60.44; H, 6.74%. Calcd for $C_{13}H_{17}ClO_3$: C, 60.82; H, 6.68%.

The chlorovinyl derivative **6** was decomposed on standing for several days to give crystals **7**, mp 147.5—148°C (lit,[7] mp 149°C); IR (Nujol mull) 3700—2100 (COOH), 1733 and 1685 (ester and carboxyl C=O) cm^{-1}.

The solid **7** was esterified with diazoethane[13] to give diethyl 2,5-difuroate whose infrared spectrum was superimposable in every detail with that of the authentic specimen.[14]

Preparation of Ethyl 5-Hexyl-2-furoates (8 and 9). Condensation of ethyl 2-furoate (23 g) with *n*-hexyl bromide (28 g) in carbon disulfide (100 m*l*) in the presence of aluminum chloride (43 g) was carried out at room temperature according to the procedure by Gilman and Calloway.[5] After being treated in the usual manner, distillation of the product gave a fraction (20 g) boiling at 110—130°C/10 mmHg. Upon fractional redistillation of the fraction using a spinning band-type distillation apparatus, two major fractions were obtained in the ratio 3:1, one was assigned to **8** (rich fraction) boiling at 142°C/20 mmHg and the other (**9**) boiling at 143°C/20 mmHg.[15] Analytical specimens (**8** and **9**) were provided by preparative vpc (Rt: 18.0 and 19.2 min, respectively). Ethyl 5-(1,1-dimethylbutyl)-2-furoate **8**, IR (neat) 3100 (=C–H), 1725 (conjugated ester C=O), 1590 (C=O), 1520 (C=C), 1300, 1135, 1016, 800, 760 cm^{-1}; NMR ($CDCl_3$) τ 2.95 (d, 1H, J=2.7 Hz, =C–H), 3.89 (d, 1H, J=2.7 Hz, =C–H), 5.67 (q, 2H, J=5.6 Hz, O–CH_2–C), 8.16—8.60 (m, 4H, –$(CH_2)_2$–), 8.64 (t, 3H, J=5.6 Hz, O–C–CH_3), 8.70 (s, 6H, *gem*-CH_3), 9.14 (t, 3H, C–CH_3).

Found: C, 69.88; H, 8.69%. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99%.

Ethyl 5-(1-methyl-1-ethylpropyl)-2-furoate **9**, IR (neat) 3100, 1725, 1590, 1520, 1300, 1135, 1018, 760 cm^{-1}; NMR ($CDCl_3$) τ 2.93 (d, 1H, J=2.7 Hz, =C–H), 3.87 (d, 1H, J=2.7 Hz, =C–H), 5.67 (q, 2H, J=5.6 Hz, O–CH_2–C), 8.32 (m, 4H, *gem*-CH_2–C), 8.65 (t, 3H, J=5.6 Hz, O–C–CH_3), 8.78 (s, 3H, C–CH_3), 9.26 (t, 6H, J=6.2 *gem*-C–CH_3).

Found: C, 69.59; H, 9.31%. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99%.

Hydrolysis of Ethyl 5-(1,1-Dimethylbutyl)-2-furoate (8). A mixture of **8** (5 g), potassium hydroxide (1.8 g), and ethanol (7 m*l*) with a few drops of water was heated at 80°C for 30 min with stirring, then poured into 100 m*l* of ice water and acidified with dilute sulfuric acid to give **10** (3.1 g), mp 60.5°C (crude); IR (Nujol mull) 1689 (carboxylic acid C=O), 1600 (C=C), 1528, 1310, 1160, 1019 cm^{-1}. By treating **10** with diazomethane, methyl 5-(1,1-dimethylbutyl)-2-furoate was obtained, bp 91—92°C/4 mmHg. Purification of the methyl ester of **10** was performed by preparative vpc: IR (neat) 3150, 1735, 1593, 1520, 1308, 1142, 1022, 990, 926, 795, 760 cm^{-1}.

Found: C, 68.43; H, 8.72%. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63%.

Electrolysis Apparatus. The electrolysis cell was a

11) All melting and boiling points are uncorrected. Preparative gas chromatography was operated by a partially modified Yanagimoto GCG-550T type apparatus fitted with 10% coated SE-30 packed column, 3 m long, carrier gas H_2 20 m*l*/min at 130—175°C. Infrared spectra were determined with a Hitachi EPI-S2 spectrophotometer. NMR spectra were obtained on a Japan Electron Optics Laboratory spectrometer (JNM-C-60) in deuteriochloroform with TMS as an internal reference. Microanalyses were carried out by Miss M. Harada of our laboratory.

12) A. Girard and G. Sandulesco, *Helv. Chim. Acta*, **19**, 1095 (1936).

13) B. Eistert and L. Klein, *Chem. Ber.*, **101**, 900 (1968).

14) R. Andrisano, *Ann. Chim.* (Rome), **40**, 30 (1950); *Chem. Abstr.*, **45**, 7563 (1951).

15) The constitution of both fractions was estimated as follows: the former fraction contained 97% of **8** and the latter 50% of **9**, elucidated by vpc using poly-neopentyl glycol succinate 10% coated Diasolid L. M. column.

water-jacketed beaker, 3.2 cm long in diameter and 10 cm high, fitted with a gas lead pipe, a thermometer, and a magnetic stirrer. The electrodes were two platinum foils (1.5×2.0 cm^2) about 1 mm apart from each other. Current was controlled by manually adjusting the applied voltage as required. The direction of current was changed every 30 sec by means of a commutator.

Electrolysis of 5-n-*Hexyl-2-furoic Acid (**4**) in Acetic Acid-Methanol-Water.* A solution of **4** (1.5 g), potassium hydroxide (0.65 g) in acetic acid (20 ml)-methanol (15 m*l*)-water (10 m*l*) was electrolyzed at 29—34°C for 26 hr under a current of 0.8—1.2 A at 16—17 V (Experiment 1, Table 1). 10 m*l* of acetic acid was added every 4 hr. The reaction mixture was poured into 200 m*l* of ice water and extracted with ether. The ethereal solution was washed with aqueous sodium bicarbonate followed by aqueous sodium chloride and dried over Na_2SO_4. Evaporation of the solvent gave 1.2 g of neutral product, whose vpc analysis showed presence of two main constituents (Rt min, peak area%): **11** (14.2, 28) and **12** (15.4, 46), along with minor constituents (total peak area 26%) as shown in Table 2. Analytical specimens (**11** and **12**) were obtained by preparative vpc. IR spectrum and retention time of **11** on vpc were identical with those of authentic sample.[4] The physical data of **12** together with microanalytical results are as follows: IR (neat) 3100 (=C–H), 1830 (shoulder), 1779 (lactone C=O), 1613, 1463, 1171, 912, 822 cm^{-1}; NMR ($CDCl_3$) 2.90 (d, 1H, J=5.6 Hz, =C–H), 3.79 (d, 1H, J=5.6 Hz, =C–H), 6.88 (s, 3H, O–CH_3), 7.90—8.30 (m, 2H, C–CH_2–C–C=C–C=O), 8.73 (broad, 8H, –$(CH_2)_4$–) and 9.14 (t, 3H, C–CH_3).

Found: C, 66.52; H, 9.32%. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15%.

The alkaline solution was acidified with dilute sulfuric acid and extracted with ether. The ethereal solution was washed with aqueous sodium chloride, dried over Na_2SO_4 and concentrated *in vacuo*. The remaining oil was treated with diazomethane to give 0.3 g of methyl ester whose vpc showed a sharp peak at Rt 14 min (peak area 60%) along with many minor peaks. The major constituent after purified by preparative vpc was identical with that of authentic sample **11**.

In a similar manner, electrolysis of 5-(1,1-dimethylbutyl)-2-furoic acid **10** in acetic acid-methanol-water media, as seen in Experiment 4, gave 2.0 g of neutral and 0.5 g of acidic portions. Vpc analysis of the neutral portion showed presence of three main compounds (Rt min, peak area%): **15** (11.7, 5), **16** (13.6, 18) and **17** (28.6, 30) along with many minor constituents. From the acidic portion, 0.5 g of methyl ester was obtained after being treated with diazomethane. Vpc analylysis showed a sharp peak (Rt 11.7 min, peak area 61%) and minor peaks (total 10 peaks). IR spectrum of the main component, after being purified by preparative vpc, was identical with that of **15**. Compound **15**: IR (neat) 1745 (ester C=O), 1709 (ketone C=O), 1471, 1440, 1369, 1213, 1170, 1090, 840 cm^{-1}; NMR ($CDCl_3$) τ 6.32 (s, 3H, O–CH_3), 7.30 (m, 4H, CO–$(CH_2)_2$–CO), 8.11—8.90 (broad, 4H, –$(CH_2)_2$–), 8.86 (s, 6H, *gem*-CH_3), 9.10 (t, 3H, C–CH_3).

Found: C, 66.01; H, 10.04%. Calcd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07%.

Compound **16**: IR (neat) 3100 (=C–H), 1830 (shoulder), 1778 (lactone C=O), 1613, 1134, 1108, 914, 826 cm^{-1}; NMR ($CDCl_3$) τ 2.80 (d, J=6.0 Hz, 1H, =C–H), 3.70 (d, J=6.0 Hz, 1H, =C–H), 6.83 (s, 3H, O–CH_3), 8.65 (m, 4H, –CH_2–), 9.03 (s, 9H, $3CH_3$).

Found: C, 66.70; H, 9.46%. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15%.

Compound **17**: IR (neat) 3100 (=C–H), 1786, 1760 (acetoxy, lactone C=O), 1619, 1394, 1372, 1333, 1223, 1124, 1097, 1055, 1015, 992, 913, 840, 820, 736 cm^{-1}; NMR ($CDCl_3$) τ 2.56 (d, 1H, J=6.0 Hz, =C–H), 3.71 (d, 1H, J=6.0 Hz, =C–H), 7.92 (s, 3H, O–CO–CH_3), 8.65 (m, 4H, –$(CH_2)_2$–), 8.98—9.03 (s, 9H, $3CH_3$).

Found: C, 63.50; H, 8.47%. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02%.

Electrolysis of 5-*n-Hexyl-2-furoic acid (**4**) in Acetic Acid.* A solution of **4** (1.0 g) and potassium acetate (0.6 g) in acetic acid (35 m*l*) was electrolyzed at 28—35°C for 8 hr under a current of 0.2—0.3 A at 50 V (Experiment 2, Table 1). After the usual working-up, 0.8 g of neutral oily material was obtained. Vpc analysis showed presence of a major constituent **13** (Rt: 29.0 min, peak area 71%) along with minor constituents (total 12 peaks). Analytical specimen **13** provided by preparative vpc has following physical constants: IR (neat) 3100 (=C–H), 1781, 1750 (acetate and lactone C=O), 1383, 1220, 816 cm^{-1}; NMR ($CDCl_3$) τ 2.42 (d, 1H, J=5.6 Hz, =C–H), 3.79 (d, 1H, J=5.6 Hz, =C–H), 7.91 (s, 3H, O–CO–CH_3), 8.68 (broad, 10H, 5–CH_2–), 9.11 (t, 3H, C–CH_3).

Found: C, 63.86; H, 8.17%. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02%.

Electrolysis of 5-n-*Hexyl-2-furoic Acid (**4**) in Aqueous Methanol.* A solution of **4** (0.9 g) and potassium hydroxide (0.3 g) in 66% aqueous methanol (30 m*l*) was electrolyzed at 25—26°C for 2 hr under a current of 1 A at 15 V (Experiment 3, Table 1). After the usual working-up, 0.7 g of neutral and 0.5 g of crystalline acidic portions were obtained. Analytical data of the neutral portion are shown in Table 2. An acid, mp 64—65°C (*n*-hexane) (lit,[4] mp 60—60.5°C), treated with diazomethane, gave the corresponding methyl ester whose IR spectrum and retention time on vpc coincided with those of authentic sample **11**. Similarly, electrolysis of 5-(1,1-dimethylbutyl)-2-furoic acid **10** in acetic acid-methanol-water media and in aqueous methanol were carried out (Experiments 5 and 6). These results are also shown in Table 2.

Methyl 5-n-*Hexyl-2,5-dimethoxy-2,5-dihydro-2-furoates (**19a** and **19b**).* A solution of methyl 5-*n*-hexyl-2-furoate (1.1 g) in 25 m*l* of methanol containing two drops of concentrated sulfuric acid was electrolyzed with platinum electrodes at 20°C for 6 hr under a current density of 0.06 A/cm^2 at 15.5—16 V. The reaction mixture was concentrated *in vacuo* and extracted with ether. The ethereal solution was washed with aqueous sodium chloride and then concentrated *in vacuo*. Distillation of the residue gave 1.3 g of oil, bp 115—120°C/2.5 mmHg, consisting of two products (Rt 11.5 and 12.8 min in a ratio of 1:0.7). Isolation of two stereoisomers of methyl 5-*n*-hexyl-2,5-dimethoxy-2,5-dihydro-2-furoates was carried out by preparative vpc; **19**b (*cis* isomer) Rt: 11.5 min, **19a** (*trans* isomer) Rt: 12.8 min. *trans* Isomer **19a**, IR (neat) 3100 (=C–H), 1755 (ester C=O), 1635 (C=C), 1465, 1442, 1260, 1064, 1035, 857, 794 cm^{-1}; NMR ($CDCl_3$) τ 3.91 (s, 2H, =C–H), 6.17 (s, 3H, –CO–O–CH_3), 6.61 (s, 3H, O–CH_3), 6.80 (s, 3H, O–CH_3), 8.20 (m, 2H, C–CH_2–C–C=C–C=O), 8.68 (m, 8H, 4–CH_2–), 9.10 (t, 3H, C–CH_3).

Found: C, 61.65; H, 9.00%. Calcd for $C_{14}H_{24}O_5$: C, 61.75; H, 8.88%.

cis-Isomer **19**b: IR (neat) 3100 (=C–H), 1755 (ester C=O), 1635 (C=C), 1465, 1442, 1340, 1270, 1160—1000, 940, 859, 794 cm^{-1}; NMR ($CDCl_3$) τ 3.91 (s, 2H, =C–H), 6.17 (s, 3H, CO–O–CH_3), 6.55 (s, 3H, O–CH_3), 6.70 (s, 3H, O–CH_3), 8.15 (m, 2H, C–CH_2–C–C=C–C=O), 8.68 (broad, 8H,

4-CH_2-), 9.10 (t, 3H, C-CH_3).

Found: C, 61.65; H, 8.96%. Calcd for $C_{14}H_{24}O_5$: C, 61.75; H, 8.88%.

Hydrolysis of Methyl 5-n-Hexyl-2,5-dimethoxy-2,5-dihydro-2-furoate. A solution of 0.5 g of **19**, potassium hydroxide (0.1 g) and two drops of water in methanol (2.2 m*l*) was stirred at room temperature for 24 hr. The mixture was poured into 25 m*l* of ice water, neutralized with acetic acid to pH 7.0—7.5 and extracted with ether. The extracts, after being concentrated in *vacuo*, gave a trace of oil whose vpc chart showed no peak corresponding to **19**. The aqueous solution was acidified to pH 4—5 with dilute sulfuric acid. Carbon dioxide was evolved. The organic layer was taken up in ether, washed with aqueous sodium bicarbonate and aqueous sodium chloride and concentrated in *vacuo*. The residue (0.25 g) contained a constituent corresponding to the γ-keto ester **11** (peak area 85% on vpc). IR spectrum of the analytical specimen coincided well with that of authentic sample mentioned in the preceeding paragraph. The alkaline solution was acidified with dilute sulfuric acid, taken up in ether, washed with aqueous sodium chloride and concentrated in *vacuo*, giving 1.5 g of oily material. On treatment with diazomethane the corresponding methyl ester **11** was obtained.

Electrolysis of the alkaline solution obtained by hydrolysis of **19** was carried out as follows: to a methanol solution prepared from 0.5 g of **19**, 1.0 g of potassium hydroxide and 2.2 m*l* of methanol with a few drop of water, 12.8 m*l* of methanol and 5 m*l* of water were added (in total methanol 15 m*l*, water 5 m*l*). The solution was electrolyzed at 23—27°C for 0.5 hr under a current of 0.33 A at 14.4—15 V. The reaction solution was concentrated in *vacuo*, poured into 25 m*l* of ice water, neutralized with acetic acid to pH 7.0—7.5 and extracted with ether. Evaporation of the solvent gave 0.28 g of neutral portion whose vpc data are very similar to those of Experiment 3 in Table 2. The aqueous solution was acidified with dilute sulfuric acid and extracted with ether. After the usual working-up, the ethereal solution gave a crystal (0.05 g): mp 64.5—65°C from *n*-hexane (lit,[4] mp 60—60.5°C). The crystal was treated with diazomethane to give **13** whose retention time on vpc and IR spectrum are identical with those of the specimen mentioned in the paragraph above.