

ELECTROOXIDATION OF 2-ARYLFURANS

Miroslav JANDA, Jan ŠROGL, Hana DVOŘÁKOVÁ, Dalimil DVOŘÁK and Ivan STIBOR

*Department of Organic Chemistry,**Prague Institute of Chemical Technology, 166 28 Prague 6*

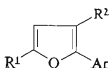
Received February 29th, 1980

Electrochemical methoxylation of 2-phenylfuran (*I*) and 2-(4-nitrophenyl)furan (*VI*) proceeded anomalously, affording 5-methoxy-2-phenylfuran (*XI*) and 5-methoxy-2-(4-nitrophenyl)furan (*XIII*), respectively. 2-Phenyl-5-methylfuran (*II*) and methyl-2-(2-methylphenyl)-3-furoate (*VIII*) behaved normally giving the respective 2,5-dimethoxy-2,5-dihydrofuran derivatives *XII* and *XIV*. The suggested $EC_N EC_B$ mechanism of the anomalous methoxylation was confirmed by methoxylation of compound *II*, in which the methyl group hinders the last C_B step, and also of compound *VIII* in which the aromaticity is suppressed by forced deviation from planarity. Forced deviation from planarity was moreover studied also on 2-(4-methylphenyl)furan (*III*), 5-methyl-2-(2-methylphenyl)furan (*IV*) and 3,5-dimethyl-2-(2-methylphenyl)furan (*V*) as model compounds. For all the derivatives the INDO charges were calculated and correlated with the 1H - and ^{13}C -NMR spectra. The experimental electronic spectra were correlated with the theoretical ones (INDO-S-CI). All the results obtained confirm the suggested mechanism.

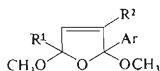
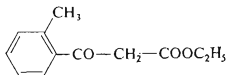
In our studies on the Clauson-Kaas electrochemical methoxylation of 2-phenylfuran (*I*) we described an anomalous course of this reaction¹, leading exclusively to 5-methoxy-2-phenylfuran (*XI*) instead of to the usual substituted 2,5-dimethoxy-2,5-dihydrofuran derivatives. We suggested that this reaction proceeds by an $EC_N EC_B$ mechanism, in which the last chemical step (C_B) consists in the loss of proton at $C_{(5)}$ of the furan ring, the driving force of the whole process being conjugation of substituent in position 2 with the arising furan heteroaromatic system. In order to prove our assumptions, we studied the reaction in more detail using the following two approaches: 1) The proton loss in the re-aromatization step was prevented by the presence of methyl group in 2-phenyl-5-methylfuran (*II*); 2) the aromaticity of the phenyl group in the side chain was suppressed by its forced deviation from coplanarity with the furan ring; this we assume to take place in methyl 2-(2-methylphenyl)-3-furoate (*VIII*). Since forced deviation from coplanarity in compounds of this type has not been hitherto studied, we prepared several model compounds. The present paper summarizes our results.

The starting compound *I* was synthesized from furan by the described^{2,3} method, compounds *II*–*VII* were prepared in 5–32% yields by a modified procedure⁴. The arylation of the furan derivatives generally affords low yields of the desired products. A recent paper⁵ reports higher yields, however, the described method is

more complicated and has not been applied to *ortho*-substituted derivatives. Compounds with greater steric demands do not react at all. For this reason, methyl 2-(2-methylphenyl)-3-furoate (VIII) was prepared by a modified Feist-Bennary synthesis⁶. Methyl 2-methylbenzoate was transformed by Claisen condensation into the keto ester IX which reacted with chloroacetaldehyde in pyridine. The crude mixture of esters was purified by saponification with sodium hydroxide and the obtained acid was again transformed into the ester with diazomethane (the overall yield was less than 10%). 2-(4-Acetamidophenyl)furan (X) was obtained by reaction of compound VI with hydrazine and Raney nickel.



- I, Ar = C₆H₅, R¹ = R² = H
 II, Ar = C₆H₅, R¹ = CH₃, R² = H
 III, Ar = *p*-CH₃C₆H₄, R¹ = R² = H
 IV, Ar = *o*-CH₃C₆H₄, R¹ = CH₃, R² = H
 V, Ar = *o*-CH₃C₆H₄, R¹ = R² = CH₃
 VI, Ar = *p*-NO₂C₆H₄, R¹ = R² = H
 VII, Ar = *p*-BrC₆H₄, R¹ = R² = H
 VIII, Ar = *o*-CH₃C₆H₄, R¹ = H, R² = COOCH₃
 X, Ar = *p*-CH₃CONHC₆H₄, R¹ = R² = H
 XI, Ar = C₆H₅, R¹ = OCH₃, R² = H
 XIII, Ar = *p*-NO₂C₆H₄, R¹ = OCH₃, R² = H



- XII, Ar = C₆H₅, R¹ = CH₃, R² = H
 XIV, Ar = *o*-CH₃C₆H₄, R¹ = H, R² = COOCH₃

The electrochemical methoxylations were carried out under galvanostatic conditions using the standard procedure^{7,8}. Better experimental results were obtained with a platinum, rather than carbon anode. Ammonium bromide was used as the auxiliary electrolyte. The low preparative yields (15–30%) reflected the instability of the starting arylfurans as well as the products of their electrochemical methoxylation. Results of the electrochemical experiments are summarized in Table I.

The formation of anomalous reaction products XI and XIII is in accord with the proposed EC_NEC_B mechanism. It was found^{9,10} that a nitro group in *para*-position enhances the acidity of the hydrogen in position 5 of the furan nucleus. Methoxylation of compound II, in which the proton cleavage is made impossible by the presence of methyl group, afforded solely the "normal" 2,5-dimethoxy-2,5-dihydroxyfuran

TABLE I
Electrochemical Methoxylations of Arylfurans

| Compound mmol | Electrodes electrolyte | Current (A) mount of electricity, F mol ⁻¹ | Product yield, % |
|----------------------|---|---|---------------------------------|
| <i>I</i> (55.6) | C ⁺ Ni ⁻ NH ₄ Br | 1.5 1.0 | <i>XI</i> 21.8 conv. 71% |
| <i>I</i> (17) | Pt ⁺ Ni ⁻ NH ₄ Br | 1.0 4.4 | <i>XI</i> ^a |
| <i>II</i> (19) | Pt ⁺ C ⁻ NH ₄ Br | 0.5 3.4 | <i>XII</i> 26.3 |
| <i>VI</i> (10) | Pt ⁺ C ⁻ NH ₄ Br | 0.5 5.1 | <i>XIII</i> 13.8 |
| <i>VIII</i> (4.0) | Pt ⁺ C ⁻ NaClO ₄ | 0.5 7.7 | <i>XIV</i> ^a |
| <i>VIII</i> (4.2) | Pt ⁺ C ⁻ NH ₄ Br | 0.5 28 | <i>XIV</i> 20 ^{b,c} |

^a Product identified only by thin-layer chromatography; ^b recovered 61% of the starting *VIII*;
^c purity 95%, the main impurity is probably a product of replacement of one of the methoxyl group
by bromine.

TABLE II
¹³C-NMR Shifts (in ppm) Compounds *II*–*IV*, *VI* and *VII*

| Position | <i>II</i> ^a | <i>III</i> ^b | <i>IV</i> ^c | <i>VI</i> | <i>VII</i> |
|----------|------------------------|-------------------------|------------------------|-----------|------------|
| 1 | 151.89 | 141.70 | 151.34 | 144.25 | 142.33 |
| 2 | 107.84 | 111.67 | 109.57 | 112.48 | 111.76 |
| 3 | 105.93 | 104.38 | 107.57 | 109.03 | 105.57 |
| 4 | 152.53 | 154.44 | 151.98 | 151.82 | 152.98 |
| 5 | 131.41 | 128.50 | 130.69 | 136.51 | 129.78 |
| 6 | 123.405 | 123.95 | 134.05 | 124.32 | 121.04 |
| 7 | 128.68 | 129.41 | 131.14 | 124.04 | 125.31 |
| 8 | 136.77 | 137.06 | 126.95 | 146.46 | 131.78 |
| 9 | 128.68 | 129.41 | 126.68 | 124.04 | 125.31 |
| 10 | 123.405 | 123.95 | 125.95 | 124.32 | 121.04 |

^a CH₃ — 13.55; ^b CH₃ — 21.11; ^c CH₃ — 13.47 and 21.84.

derivative *XII*. This confirmed that an anomalous reaction course unconditionally requires the presence of a hydrogen atom in position 5.



TABLE III
INDO Charges on C and H Atoms in Compounds I—VI and VIII

| Position | I | | II | | III | | IV | |
|----------|--------|--------|--------|--------|--------|--------|--------|--------|
| | C | H | C | H | C | H | C | H |
| 1 | 0.148 | -0.021 | 0.166 | — | 0.147 | -0.022 | 0.154 | — |
| 2 | -0.036 | -0.006 | -0.055 | -0.006 | -0.035 | -0.007 | -0.049 | -0.007 |
| 3 | -0.051 | -0.047 | -0.047 | -0.004 | -0.053 | -0.003 | -0.066 | -0.007 |
| 4 | 0.161 | — | 0.155 | — | 0.163 | — | 0.169 | — |
| 5 | 0.016 | — | 0.017 | — | 0.101 | — | 0.002 | — |
| 6 | 0.018 | -0.020 | 0.016 | -0.027 | 0.021 | -0.027 | 0.037 | — |
| 7 | 0.027 | -0.026 | 0.028 | -0.026 | 0.013 | -0.026 | -0.013 | -0.025 |
| 8 | 0.022 | -0.025 | 0.021 | -0.026 | 0.035 | — | 0.028 | -0.026 |
| 9 | 0.026 | -0.026 | 0.026 | -0.026 | 0.013 | -0.027 | 0.019 | -0.025 |
| 10 | 0.022 | -0.026 | 0.019 | -0.020 | 0.025 | 0.021 | 0.027 | -0.028 |

| Position | V | | VI | | VIII | |
|----------|--------|--------|--------|--------|--------|--------|
| | C | H | C | H | C | H |
| 1 | 0.159 | — | 0.155 | -0.016 | 0.135 | -0.015 |
| 2 | -0.062 | -0.006 | -0.036 | -0.001 | -0.019 | 0.002 |
| 3 | -0.041 | — | -0.040 | 0.000 | -0.133 | — |
| 4 | 0.152 | — | 0.153 | — | 0.228 | — |
| 5 | 0.004 | — | 0.015 | — | -0.003 | — |
| 6 | 0.037 | — | 0.022 | — | 0.048 | — |
| 7 | 0.013 | -0.025 | 0.029 | 0.015 | 0.012 | -0.021 |
| 8 | 0.028 | -0.026 | 0.026 | — | 0.036 | -0.022 |
| 9 | 0.019 | -0.025 | 0.029 | 0.015 | 0.021 | -0.016 |
| 10 | 0.027 | -0.028 | 0.027 | 0.012 | 0.055 | -0.065 |

The question of affecting the aromaticity of a substituent in position 2 by forced deviation from coplanarity was more complicated. In order to check our assumptions, we calculated the electronic states of compounds *I–VI* and *VIII*. The geometry was optimized by the EHT method; the furan ring geometry was taken from microwave spectral studies¹¹ and, as well as the benzene ring geometry, was assumed to be rigid. We optimized the torsion angle between both these systems (α) and torsion angles between substituents (β , γ) with expected mutual interaction (in 15° steps). It was thus calculated that the planar arrangement corresponds to an energy minimum for compounds *I–III*, *VI* and *VII*, whereas the minimum for compounds *IV*, *V* and *VIII* is represented by conformation with a torsion angle 105°. The optimal torsion angles of the substituents were found to be 0°. For these conformations we calculated first the total charges on the single atoms by the INDO method¹². The same structures were treated also by the INDO-S-CI method^{13,14} which afforded the theoretical electronic spectra. The thus-obtained approximations of electronic states in the molecules were checked by their correlation with the experimental spectra which for similar systems proved to be useful¹⁵. We measured the ¹H- and ¹³C-NMR spectra; the proton shifts are given in the Experimental, shifts, obtained by analysis of the ¹³C-NMR spectra and interpreted using the published data¹⁶, are listed in Table II. The calculated (INDO) charges are summarized in Table III, the numbering of atoms being depicted on the 2-phenylfuran skeleton.

The ¹H-NMR shifts of the furan protons were correlated with the corresponding INDO charges (ξ). The relationship was calculated using the standard least squares method and is given together with the correlation coefficient pertinent for the significance level and the number of values correlated:

$$\xi = 8.95 \cdot 10^{-3} \delta_{1H} - 0.0515; \quad r = 0.6731, \quad r_{99} = 0.5897; \quad (n = 16).$$

Further we calculated the dependence of ¹³C-NMR shifts on the total INDO charges for all carbon atoms of the furan ring in all the compounds studied:

$$\xi = 2.539 \cdot 10^{-3} \delta_{13C} - 0.2241; \quad r = 0.9786, \quad r_{99.9} = 0.6527; \quad (n = 20).$$

Relationships between ¹³C-NMR shifts and INDO charges for all carbon atoms in each compound were also investigated. The results are summarized as a set of coefficients in the general equation

$$\xi = a \delta_{13C} + b; \quad r_{95} = 0.5760, \quad r_{99} = 0.7079; \quad (n = 10),$$

the coefficients *a* and *b* being given in Table IV. Since it is known that the INDO charges satisfactorily describe the electronic state of furan derivatives, it can be deduced that the chosen conformation is correct. We can thus justifiably assume

a forced deviation of the aromatic systems from coplanarity in compounds for which it was predicted by calculation. In Table V the calculated and found electronic spectra are compared. It is seen that, particularly for wavelengths, the fit between the calculated and experimental values is good. Fig. 1 depicts the calculated and measured UV spectrum of the ester *VIII*, for which we can infer with great probability a deviation of the aromatic nuclei from coplanarity. When we carried out electrochemical methoxylation of this compound, we isolated as the main reaction product the "normal" 2,5-dimethoxy-2,5-dihydro derivative *XIV*. This, together with the previously mentioned facts, supports the assumed $EC_N EC_B$ mechanism of methoxylation of furan derivatives, containing aromatic substituents.

TABLE IV

Dependence of the ^{13}C -NMR Shifts on the Total INDO Charges (coefficients of the correlation equations, a, b , and correlation coefficients, r)

| Compound | $a \cdot 10^3$ | b | r |
|------------|----------------|---------|--------|
| <i>I</i> | 2.554 | -0.2758 | 0.6392 |
| <i>II</i> | 2.356 | -0.0249 | 0.6426 |
| <i>III</i> | 2.435 | -0.2521 | 0.6192 |
| <i>IV</i> | 2.356 | -0.2522 | 0.5677 |
| <i>V</i> | 2.895 | -0.3332 | 0.8831 |

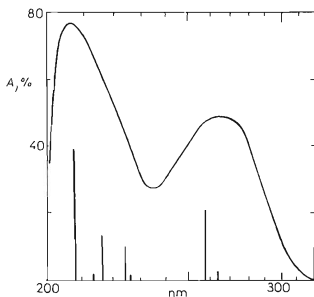


FIG. 1

Theoretical and Experimental Electronic Spectrum *VIII*

EXPERIMENTAL

Boiling and melting points are uncorrected. The analytical samples were dried for 12 h at room temperature and 67 Pa. The $^1\text{H-NMR}$ spectra were measured in deuteriochloroform on a Va-

TABLE V
Calculated and Experimental Electronic Spectra

| Compound | | λ_{max} , nm (ϵ_{max}) | | | | |
|-------------|-------|---|-----------------|-----------------|-----------------|----------------|
| <i>I</i> | exp. | 205 (11 082) | 217 (7 925) | 224 (6 616) | 278 (16 796) | 279 |
| | calc. | 205 (519) | 210 (4 670) | 227 (1 030) | 278 (822) | 279 (7 640) |
| <i>II</i> | exp. | 205 (9 589) | 222 (6 843) | 285 (17 379) | | |
| | calc. | 212 (674) | 215 (3 960) | 233 (8·50) | 279 (840) | 296 (8 640) |
| <i>III</i> | exp. | 205 (10 869) | 217 (8 754) | 280 (17 258) | | |
| | calc. | 201 (992) | 211 (3 520) | 212 (2 620) | 231 (628) | 282 (444) |
| <i>IV</i> | exp. | 210 (11 393) | 223 (9 408) | 280 (15 004) | | |
| | calc. | 211 (576) | 217 (1 290) | 242 (4 170) | 255 (3 710) | 263 (516) |
| <i>V</i> | exp. | 210 (13 177) | 270 (9 234) | | | |
| | calc. | 211 (609) | 221 (1 930) | 246 (4 850) | 263 (1 220) | 267 (3 320) |
| <i>VI</i> | exp. | 204 (12 974) | 240 (8 776) | 348 (16 118) | | |
| | calc. | 221 (1 057) | 245 (843) | 249 (3 860) | 288 (94) | 305 (7 620) |
| <i>VII</i> | exp. | 204 (9 686) | 220 (7 757) | 286 (21 540) | | |
| <i>VIII</i> | exp. | 206 (15 838) | 266 (7 256) | | | |
| | calc. | 210 (6 050) | 217 (3 215) | 224 (3 120) | 257 (3 820) | 264 (750) |
| <i>X</i> | exp. | 204 (13 214) | 218 (10 311) | 284 (25 909) | | |

rian-XL-100 (100 MHz) instrument, using tetramethylsilane as internal standard. The ^{13}C -NMR spectra were taken on a Bruker WP-80 (20.12 MHz) instrument. The chemical shifts are given in δ -units relative to tetramethylsilane. The IR spectra were recorded on a Perkin-Elmer 325 spectrophotometer in tetrachloromethane or carbon disulfide, UV spectra on a Spedcor instrument. Gas-liquid chromatography was carried out on a Chrom 31 chromatograph (flame-ionization detector, carrier gas nitrogen). Electrochemical reactions were performed in an all-glass electrolyzer (200 ml) with a platinum anode (45 cm²) and carbon cathode (2.5 × 7 cm cylinder). The temperature was maintained by external cooling, and the electrolyzer content was stirred by means of a magnetic stirrer.

2-Phenyl-5-methylfuran (*II*)

A mixture of aniline (25 g; 0.27 mol), isopentyl nitrite (55 ml) and 2-methylfuran (400 ml) was set aside at 40°C for 24 h, washed with water, dried over sodium sulfate, taken down and distilled, affording 11.3 g (26.7%) of compound *II*, b.p. 110–112°C/2 kPa. For C₁₁H₁₀O (158.2) calculated: 83.4% C, 6.32% H; found: 81.58% C, 6.54% H. ^1H -NMR spectrum: 2.35 (s, 3 H, CH₃), 6.02 (m, 1 H, H-3), 6.50 (m, 1 H, H-4), 7.15–7.70 (m, 5 H, Ar).

2-(4-Methylphenyl)furan (*III*)

A mixture of *p*-toluidine (28.9 g; 0.27 mol), isopentyl nitrite (55 ml) and furan (350 ml) was set aside at 30°C for 24 h. The mixture was washed with water, dried over sodium sulfate, taken down and distilled to give 13.6 g (31.9%) of *III*, b.p. 117–120°C/2 kPa. For C₁₁H₁₀O (158.2) calculated: 83.4% C, 6.32% H; found: 81.17% C, 6.65% H. ^1H -NMR spectrum: 2.34 (s, 3 H, CH₃), 6.43 (m, 1 H, H-4), 6.53 (m, 1 H, H-3), 7.40 (m, 1 H, H-5), 7.10, 7.18, 7.30, 7.38 (AB system, 4 H, Ar).

2-(2-Methylphenyl)-5-methylfuran (*IV*)

A mixture of *o*-toluidine (28.9 g; 0.27 mol), isopentyl nitrite (55 ml) and 2-methylfuran (400 ml) was kept at 60°C for 24 h. The above-described isolation procedure afforded 6.3 g (13.6%) of *IV*, b.p. 121–123°C/2 kPa. For C₁₂H₁₂O (172.2) calculated: 83.69% C, 7.02% H; found: 83.68% C, 7.03% H. ^1H -NMR spectrum: 2.35 (s, 3 H, 3-CH₃), 2.46 (s, 3 H, CH₃), 6.05 (m, 1 H, H-4), 6.38 (m, 1 H, H-3), 7.10–7.70 (m, 4 H, Ar).

2-(2-Methylphenyl)-2,5-dimethylfuran (*V*)

A mixture of *o*-toluidine (28.9 g; 0.27 mol), isopentyl nitrite (55 ml) and 2,4-dimethylfuran (216 g) was heated to 90°C. After the exothermic reaction had ceased, the mixture was refluxed for 3 h, washed with water, dried over potassium carbonate, taken down and the residue distilled, affording 15.8 g (31%) of *V*, b.p. 110–115°C/1.6 kPa. For C₁₃H₁₆O (188.3) calculated: 83.83% C, 7.58% H; found: 83.19% C, 7.87% H. ^1H -NMR spectrum: 2.00 (s, 3 H, 3-CH₃), 2.32 (s, 3 H, CH₃), 2.35 (s, 3 H, CH₃), 5.90 (s, 1 H, H-4), 7.10–7.30 (m, 4 H, Ar).

2-(4-Nitrophenyl)furan (*VI*)

A mixture of *p*-nitroaniline (37.3 g; 0.27 mol), isopentyl nitrite (55 ml) and furan (400 ml) was kept at 30°C for 24 h, washed with water and dried over sodium sulfate. Furan was distilled off and the residue was crystallized three times from aqueous ethanol, affording 7.2 g (14.3%) of the

yellow product, m.p. 132—133°C. For $C_{10}H_7NO_2$ (189.2) calculated: 63.49% C, 3.73% H, 7.41% N; found: 63.45% C, 3.76% H, 7.49% N. 1H -NMR spectrum: 6.52 (m, 1 H, H—4), 6.82 (m, 1 H, H—3), 7.52 (m, 1 H, H—3), 7.72, 7.80, 8.18, 8.26 (AB system, 4 H, Ar).

2-(4-Bromophenyl)furan (VII)

A mixture of *p*-bromoaniline (46.5 g; 0.27 mol), isopentyl nitrite (55 ml) and furan (400 ml) was kept at 30°C for 24 h. The mixture was washed with water, taken down and the residue was steam-distilled. Crystallization from aqueous methanol afforded 10.6 g (17.1%) of the product, m.p. 81—83°C. For $C_{10}H_7BrO$ (223.1) calculated: 53.84% C, 3.16% H, 35.83% Br; found: 54.00% C, 3.30% H, 36.00% Br. 1H -NMR spectrum: 6.42 (m, 1 H, H—4), 6.60 (m, 1 H, H—3), 7.50 (m, 5 H, H—5, Ar).

Ethyl *o*-Toluyacetate (IX)

A solution of cyclohexylisopropylamine (62.1 g) in ether (50 ml) was added to a stirred solution of Grignard reagent, prepared from magnesium (10.7 g) and ethyl bromide (29 g) in ether (300 ml). A mixture of ethyl acetate (18.4 g) and methyl *o*-toluyate (30 g) was then added in the course of 1 h. The mixture was stirred for 2 h and poured on ice (360 ml) and conc. sulfuric acid (30 ml). The precipitate was dissolved on stirring and addition of 10% sulfuric acid, the ethereal layer was separated and the aqueous one was extracted with three portions (150 ml) of ether. The combined ethereal extracts were washed with water, saturated solution of sodium hydrogen carbonate, again water, and dried over magnesium sulfate. Distillation gave 21.8 g (40.1%) of IX, b.p. 92—94°C/53 Pa. For $C_{12}H_{14}O_3$ (206.2) calculated: 69.90% C, 6.80% H; found: 69.54% C, 6.91% H. 1H -NMR spectrum: 1.22 (t, 3 H, $J = 7$ Hz), 2.54 (s, 3 H), 3.92 (q, 2 H, $J = 7$ Hz), 7.00—7.57 (m, 3 H), 7.63 (d, 1 H, $J = 7$ Hz).

Methyl 2-(2-Methylphenyl)-3-furoate (VIII)

A mixture of IX (21.5 g), chloroacetaldehyde (10 ml) and pyridine (21 ml) was set aside at room temperature for 5 days. The lower layer was separated, the upper one was acidified with dilute hydrochloric acid and extracted with ether. The ethereal extracts were dried over calcium chloride, taken down and the residue was distilled *in vacuo*, yielding 16.5 g of a fraction boiling at 102 to 109°C/80 Pa. This was hydrolyzed by boiling with sodium hydroxide (4 g) in water (10 ml) and ethanol (17 ml) for 2 h. Ethanol was evaporated, the residue acidified with conc. hydrochloric acid, the precipitate dried on air and esterified with ethereal diazomethane. Evaporation and distillation gave 3.6 g of mixture, boiling at 90—99°C/0.13 kPa. Preparative thin-layer chromatography on silica gel (benzene as eluant) afforded 2.15 g (9.5%) of VIII, m.p. 37—39°C. For $C_{13}H_{12}O_3$ (216.2) calculated: 72.21% C, 5.59% H; found: 72.12% C, 5.72% H. 1H -NMR spectrum: 2.25 (s, 3 H), 3.70 (s, 3 H), 6.81 (d, 1 H, $J = 2$ Hz), 7.10—7.38 (m, 4 H), 7.43 (d, 1 H, $J = 2$ Hz). IR spectrum: 720, 890, 930, 1010, 1045, 1070, 1145, 1155, 1165, 1195, 1300, 1410, 1445, 1465, 1520, 1595, 1615, 1720, 2960, 3020 cm^{-1} .

2-(4-Acetamidophenyl)furan (X)

A solution of VI (1.9 g) in ethanol (30 ml) was mixed with 80% hydrazine hydrate (2 ml). Raney nickel and hydrazine hydrate were added at 50°C in portions (0.1 g and 0.5 ml, respectively) until the starting compound disappeared (monitored by thin-layer chromatography on Silufol in benzene). The mixture was boiled for 30 min, the catalyst was filtered off and the filtrate

taken down *in vacuo*. Water was removed by codistillation with benzene (several times). The residue was immediately dissolved in pyridine (25 ml), mixed with acetic anhydride (1.3 ml) and set aside at room temperature for 12 h. Pyridine was distilled off *in vacuo* and the product was dried by codistillation with xylene. Crystallization from ethanol afforded 1.6 g (79.2%) of X, m.p. 185–187°C. For $C_{12}H_{11}NO_2$ (201.2) calculated: 71.63% C, 5.51% H, 6.96% N; found: 71.49% C, 5.60% H, 6.91% N. 1H -NMR spectrum: 2.11 (s, 3 H, CH_3), 6.50 (m, 1 H, H—4), 6.72 (m, 1 H, H—3), 7.57 (m, 1 H, H—5), 7.67 (m, 4 H, Ar), one exchangeable proton.

Electrochemical Methoxylations

A solution of an auxiliary electrolyte (NH_4Br or $NaClO_4$; 3 g) in methanol (150 ml) was mixed in the electrolyzer with the starting compound and the mixture was cooled to $-30^\circ C$ under stirring and protection against moisture. After passage of the corresponding amount of electricity, the mixture was adjusted to pH 8 with sodium methoxide in methanol, the solvent was evaporated *in vacuo* and the residue was taken up in ether. After drying and evaporation, the product was isolated by distillation or chromatography.

2-Phenyl-5-methoxyfuran (XI); isolated by distillation, b.p. $96-98^\circ C/0.2$ kPa, homogeneous according to thin layer chromatography (Silufol, benzene–heptane 1 : 1). For $C_{11}H_{10}O_2$ (174.2) calculated: 75.84% C, 5.78% H; found: 75.80% C, 5.66% H. 1H -NMR spectrum: 3.85 (s, 3 H, OCH_3), 5.20 (d, 1 H, $J = 4$ Hz, H—4), 6.48 (d, 1 H, $J = 4$ Hz, H—3), 7.00–7.70 (m, 5 H, Ar).

2-Phenyl-5-methyl-2,5-dimethoxy-2,5-dihydroxyfuran (XII); isolated by distillation, b.p. 90 to $92^\circ C/0.1$ kPa, homogeneous according to thin-layer chromatography (Silufol, benzene). For $C_{13}H_{16}O_3$ (220.3) calculated: 70.88% C, 7.32% H; found: 70.96% C, 7.30% H. 1H -NMR spectrum: 1.63 (s, 3 H, CH_3 —C), 3.20 (s, 3 H, OCH_3), 5.75–6.20 (m, 2 H, H—3, H—4), 7.20–7.70 (m, 5 H, Ar).

5-Methoxy-2-(4-nitrophenyl)furan (XIII); purified by preparative thin-layer chromatography (silica gel, benzene–methanol 9 : 55). For $C_{11}H_9NO_4$ (219.2) calculated: 60.27% C, 4.14% H, 6.38% N, 14.10% OCH_3 ; found: 61.26% C, 4.26% H, 6.11% N, 14.10% OCH_3 . 1H -NMR spectrum: 3.95 (s, 3 H, OCH_3), 5.34 (d, 1 H, $J = 4$ Hz, H—4), 6.77 (d, 1 H, $J = 4$ Hz, H—3), 7.55, 7.63, 8.13, 8.21 (AB system, 4 H, Ar). IR spectrum: 690, 740, 850, 1020, 1045, 1110, 1165, 1260, 1330, 1340, 1370, 1430, 1520, 1530, 1560, 1590, 1615, 1680, 1730, 2860, 2920 cm^{-1} .

Methyl 2-(2-methylphenyl)-2,5-dimethoxy-2,5-dihydro-3-furoate (XIV); isolated by column chromatography of the crude electrolysis product (silica gel, chloroform). For $C_{15}H_{18}O_5$ (278.3) calculated: 64.73% C, 6.52% H; found: 64.68% C, 6.41% H. 1H -NMR spectrum: 2.32 (s, 3 H, CH_3 —C), 3.50 (s, 3 H, OCH_3), 3.62 (s, 6 H, OCH_3), 5.06 (s, 1 H, H—4), 6.44 (s, 1 H, H—5), 6.84–7.60 (m, 4 H, Ar).

REFERENCES

1. Stibor I., Šrogl J., Janda M.: J. Chem. Soc., Chem. Commun. 1975, 397.
2. Ayres D. C., Smith J. R.: J. Chem. Soc., C 1968, 2737.
3. Johnson A.W.: J. Chem. Soc. 1946, 895.
4. Benati L., La Barba N., Tiecco M., Tundo A.: J. Chem. Soc., B 1969, 1253.
5. Fišera L., Kováč J., Komanová E., Leško J.: Tetrahedron 30, 4123 (1974).
6. Joule J. A., Smith G. F.: *Heterocyclic Chemistry*, p. 252. Van Nostrand, London 1972.
7. Weinberg N. L., Weinberg H. R.: Chem. Rev. 68, 461 (1968).

8. Elming N. in the book: *Advances in Organic Chemistry* (R. A. Raphael, E. C. Taylor, H. Wynberg, Eds), Vol. 2, p. 67. Interscience, New York 1960.
9. Krutošiková A., Kováč J., Sýkora V.: *This Journal* 39, 1892 (1974).
10. Krutošiková A., Surá J., Kováč J., Kalfus K.: *This Journal* 40, 3357 (1975).
11. Bak B., Christensen D., Dixon W. B., Hansen-Nygaard L., Andersen J. M., Schottländer M.: *J. Mol. Spectrosc.* 9, 124 (1962).
12. Pople J. A., Beveridge D. L.: *Approximative Molecular Orbital Theory*. Mc Graw-Hill, New York 1970.
13. Del Bene J., Jaffé H. H.: *J. Chem. Phys.* 48, 1907 (1968).
14. Ellis R. L., Kuehnlenz G., Jaffé H. H.: *Theor. Chim. Acta* 26, 131 (1972).
15. Stibor I., Trška P., Šrogl J., Janda M.: *This Journal* 43, 2170 (1978).
16. Dana G., Convert O., Girault J. P., Mullier E.: *Can. J. Chem.* 54, 1827 (1976).

Translated by M. Tichý.