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Torii-Type Electrosynthesis of α,β-Unsaturated Esters from Furfurylated Ethylene Glycols and Amino Alcohols

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Electrosynthesis of unsaturated esters from furan derivatives, reported by Torii et al. in 1976, is an attractive method for the valorization of furanoic platform chemicals. Nevertheless, it has received practically no attention, presumably due to specific reaction conditions including the use of expensive Pt electrodes. With the aim of expanding the application of Torii-type ester electrosynthesis, we explored the electrochemical transformation of *O*-furfuryl ethylene glycols and N-furfuryl amino alcohols to esters **5**. These can be obtained in two consecutive electrochemical steps: bis-alkoxylation of the furan derived substrates **3** to give spirocycles **4**, followed by ring-opening involving oxidative fragmentation of the C–C bond. Both steps can be carried out at ambient conditions, using inexpensive graphite electrodes; however, each step required a different supporting electrolyte and acidic additive to achieve good yields of the product. Additionally, conditions were found for efficient one-pot transformation of N-furfuryl amino alcohols to esters **5** while O-furfuryl ethylene glycols under the same conditions gave esters **5** in moderate yields.

Introduction

The utilization of biomass has received increasing attention as an alternative to replace the dwindling fossil resources for the production of value-added products.[1] Biomass-derived platform chemicals are central to this initiative. Among them, furanoics, accessible in bulk amounts from lignocellulosic feedstocks, are versatile starting materials to achieve a range of chemicals with an application in material science, drug discovery, and agriculture.[2] Electrochemistry has been demonstrated as a useful tool for valorization of biomass-derived compounds.[3] Furanoics are particularly suitable substrates for electrochemical functionalization due to the low oxidation potential of the furan ring[4] (see also Supporting Information). Notable examples include oxidative dihydroxylation[5] and dialkoxylation[6] of furan derivatives. Anodic oxidative dialkoxylation was also employed in electrochemical synthesis of unsaturated ester **2** from furfuryl alcohol **1a**, furfural **1b**, and 2-furoic acid **1c** in the presence of methanol, first demonstrated by Torii *et al* (Figure 1).[7] According to their proposed mechanism, oxidative dimethoxylation of the furan ring leads to intermediate **A**. Further oxidation leads to cleavage of the *C–C* bond resulting in oxonium ion **B** and subsequent ring opening by methanol gives ester **2**. Despite the high potential value of the Torii ester electrosynthesis products, surprisingly limited application of this transformation has been demonstrated in the scientific literature.[8] Our work was focused on the electrochemical oxidation of furylmethyl derivatives **3** bearing hydroxyl group as an internal nucleophile (Figure 1). In this case, oxidative methoxylation should provide spirocyclic derivatives **4** which would undergo fragmentation to give products **5** with functionalized ester moiety. These products are valuable building blocks for further chemical transformations, including tailored polymer synthesis.

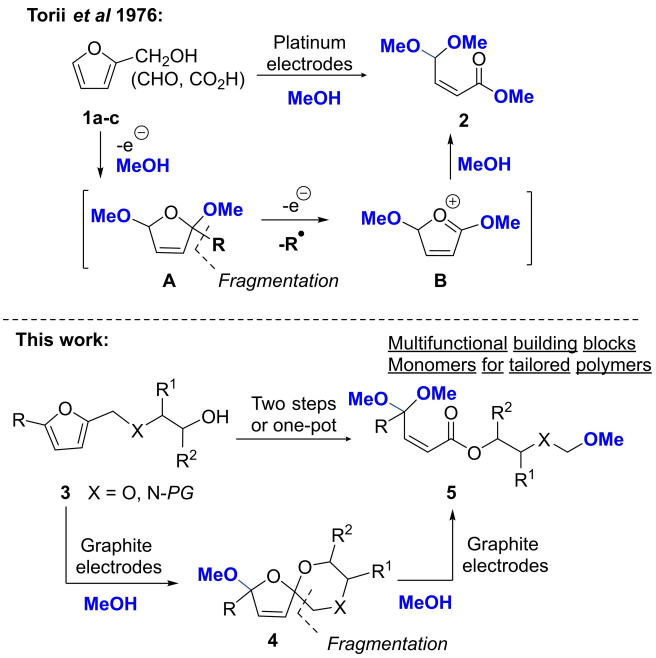

Figure 1. Torii-type electrosynthesis of unsaturated esters.

Results and Discussion

O-Furfuryl ethylene glycol (**3a**) was used as the model substrate to find efficient conditions for the spirocycle (**4a**) formation by

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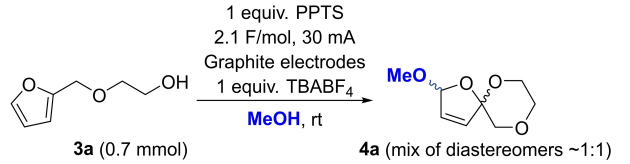
electrochemical oxidation of the furan ring (Table 1). The reaction previously has been described using one-pot two-step transformation which includes electrochemical bromination of furan using NH_4Br and a carbon anode/nickel cathode, followed by addition of sodium methoxide.[9] Given the low oxidation potential of furan, we explored direct spirocycle formation[6a] with a simple electrochemical setup using undivided cell and graphite electrodes. Methanol was used as a solvent and proton reduction as the cathode reaction. We found that the addition of PPTS (1 equiv.) was beneficial to achieve a good yield of the product **4a** (Table 1, entry 1). Decreasing or increasing the amount of PPTS led to a reduced yield of the product **4a** (Table 1, entries 2–4). It can be hypothesized that the addition of PPTS prevents formation of methoxide as the reduction product of methanol which may decrease the dimethoxylation of furane favoring formation of spirocycle **4a**.[6a] A slight increase of the total charge passed through the solution (measured in faradays per mole of substrate (F/mol)) led to a slightly higher yield (Table 1, entry 5), while significant increase of the charge was detrimental to the product **4a** formation (Table 1, entry 6). $LiClO_4$ as an electrolyte was less efficient compared to $TBABF_4$ (Table 1, entry 7). If HFIP was used as an additive instead of PPTS, a relatively good yield of product **4a** was observed at increased charge. However, in this case, a significant amount of ester **5a** formed as a by-product (Table 1, entry 8). If HFIP was used as an additive and $LiClO_4$ as an electrolyte, poor yield of spirocycle **4a** was obtained due to competing dimethoxylation of the furane (Table 1, entry 9). Optimal conditions were suitable also for the oxidation of alcohol **3a** to spirocycle **4a** in 0.5 g scale (Table 1, entry 10).

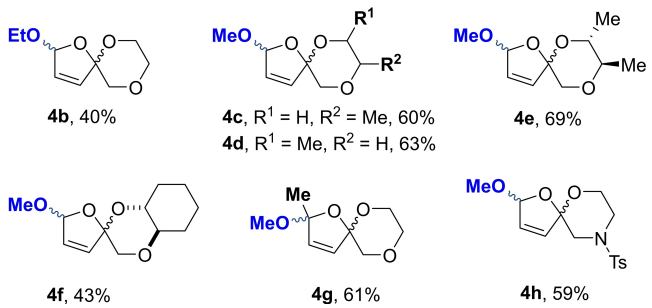
Table 1. Oxidative cyclization of alcohol **3a** to spirocycle **4a**.



3a (0.7 mmol) **4a** (mix of diastereomers ~1:1)

Entry	Conditions[a]	Yield of **4a**[b]
1	none	70%
2	no PPTS	50%
3	0.5 equiv. PPTS	58%
4	2.0 equiv. PPTS	55%[c]
5	2.5 F/mol	77%
6	4.0 F/mol	59%
7	$LiClO_4$ instead of $TBABF_4$	59%
8	no PPTS, 20 equiv. HFIP, 4 F/mol	52%[d]
9	no PPTS, 20 equiv. HFIP, $LiClO_4$ instead of $TBABF_4$,	38%[e]
10	45 mA, 500 mg scale	71%

[a] Deviation from the conditions given in the scheme. [b] Isolated yields are given; [c] Precipitate deposition on cathode observed; [d] Formation of **5a** was observed, isolated yield 15%. [e] dimethoxylation product of furane is a major by-product according to ^{1}H-NMR of a crude mixture



4b, 40% **4c**, R^1 = H, R^2 = Me, 60% **4d**, R^1 = Me, R^2 = H, 63% **4e**, 69%

4f, 43% **4g**, 61% **4h**, 59%

Scheme 1. Scope of spirocycle **4** synthesis.

The scope for spirocycle **4b–h** synthesis was investigated for a wider range of ethylene glycol and amino ethanol derivatives **3a–h** bearing furfuryl substituent (Scheme 1). Ethanol was also found to be a competent nucleophile to form ethoxy-substituted product **4b**, although in a lower yield than **4a** formed with methanol as nucleophile. Moreover, electrolysis in ethanol led to precipitate formation on the cathode. Substitution at ethylene glycol linker in starting materials **3c–f** gave products **4c–f** with good yields. Methyl substitution at furan 5th position in the starting material did not significantly affect the yield of the product **4g**. *N*-substituted amino ethanol derivative **3h** was also subjected to electrochemical cyclization to give spirocycle **4h** in good yield.

With spirocycles **4** in hand, their electroxidative fragmentation was investigated with an aim to obtain esters **5**. Spirocycle **4a** was used as a model compound to establish the conditions for this step (Table 2). PPTS as an additive and $TBABF_4$ as an electrolyte used for spirocycle **4a** formation were not suitable for obtaining ester **5a** due to precipitation of the PPTS decomposition products on the cathode during prolonged electrolysis (Table 2, Entry 1).

When acetic acid and HFIP were used as additives, the yield of product **5a** was considerably increased, however, the formation of an inseparable side-product along ester **5a** was observed (Table 2, entry 2). To obtain ester **5a** in a good yield, AcOH (4 equiv.) as an additive and $LiClO_4$ as electrolyte were

Table 2. Conditions for the oxidative fragmentation of spirocycle **4a**.

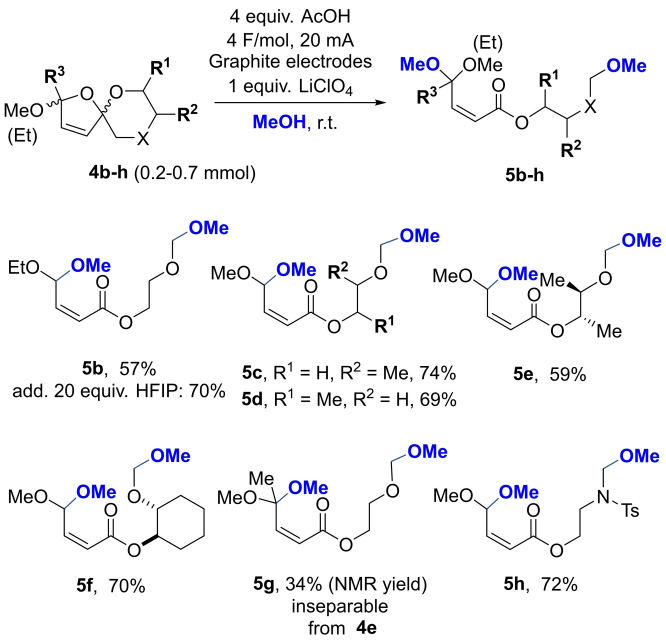
4a (0.6 mmol) **5a**

Entry	Conditions[a]	Yield of **5a**[b]
1	1 equiv. PPTS instead of AcOH $TBABF_4$ instead of $LiClO_4$	9%[c]
2	Add 20 equiv. HFIP $TBABF_4$ instead of $LiClO_4$	58%[d]
3	None	68% (77%)[e]
4	no AcOH	11%
5	1 equiv. AcOH	58%
6	2 equiv. AcOH	55%
7	add. 20 equiv. HFIP	67%
8	2.0 F/mol	(59%)[e,f]
9	3.0 F/mol	(74%)[e,g]

[a] Deviation from the conditions given in the scheme. [b] Isolated yields are given if not indicated otherwise. [c] Unreacted starting material (isolated yield: 55%). [d] Contains unidentified inseparable by-product ~15% [e] ^{1}H-NMR-yield using 1,4-bis(trichloromethyl)benzene as an internal standard. [f] Unreacted starting material (^{1}H-NMR yield: 20%) [g] Unreacted starting material (^{1}H-NMR yield: 5%).

found to be crucial reaction components (Table 2, Entry 3). Decreasing the amount of AcOH reduced the yield of product **5a** (Table 2, Entries 4–6). Addition of HFIP did not have an impact on product **5a** formation (Table 2, Entry 7). Notably, 4.0 F/mol of charge were needed to achieve complete consumption of the starting material **4a** (Table 2, Entries 8,9). This indicated a parallel competitive oxidation process since in theory only 2.0 F/mol are needed for the desired transformation (*vide infra*). In all the experiments, the formation of ester **5a** with a Z-configuration double bond was observed while *E*-isomer formation was not detected. *Z*-Configuration of ester **5a** was confirmed by characteristic coupling constant of double bond protons (J = 11.8 Hz) and their cross peaks in NOESY spectra (see Supporting Information)

Spirocycles **4b–h** were subjected to electrochemical oxidative fragmentation to esters **5b–h** using the optimized conditions found for model substrate **4a** (Scheme 2). Ethoxy substituted spirocycle **4b** gave product **5b** in a slightly lower yield compared to the methoxy analogue **5a**. Noteworthy, mixed acetal **5b** formed exclusively, indicating that no transacetalyzation with methanol takes place during the reaction. Addition of HFIP to the reaction of substrate **4b** improved the yield of product **5b** – such an effect was not observed in the reaction of the model substrate **4a** (Table 2, entry 8). Substrates **4c–f** with a substituted ethylene linker gave the desired esters **5c–f** in good yields using standard conditions with no HFIP additive. Methyl substituted substrate **4g** also gave the expected product **5g**, however, it was difficult to separate from the unreacted starting material. In this case full conversion of spirocycle **4g** could not be achieved after 4.0 F/mol of charge passed. Morpholine derivative **4h** was efficiently transformed to the *O*-acylated *N*-protected amino alcohol **5h**.

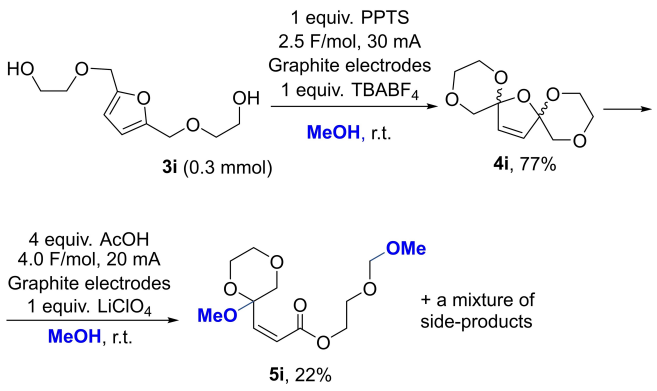


Scheme 2. Scope of oxidative fragmentation of spirocycles **4** to esters.

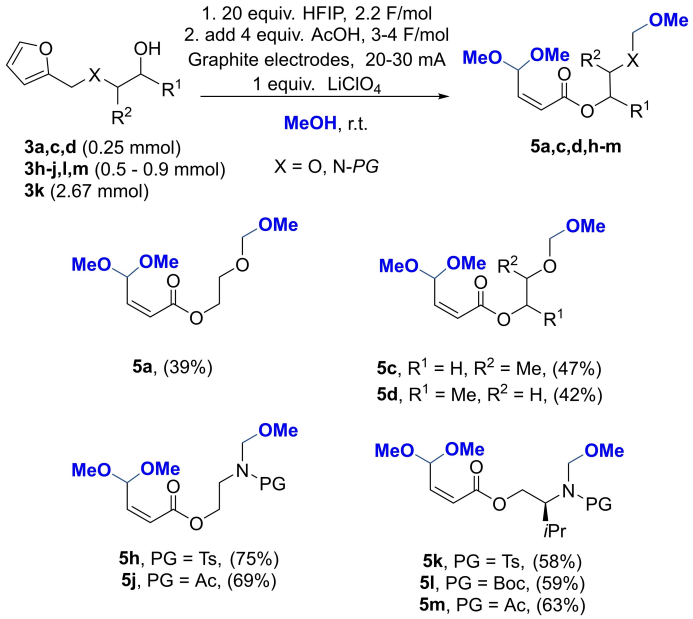
Diol **3i** derived from bis-hydroxymethylfuran was also successfully transformed into the spirocycle **4i** by anodic oxidation (Scheme 3). However, electrochemical oxidative fragmentation of the spirocycle **4i** gave the expected product **5i** in a relatively low yield (22%).

One-pot synthesis of esters **5** from alcohols **3** was also explored (Scheme 4). PPTS additive which was found beneficial for the transformation of substrates **3** to spirocycles **4** could not be applied for this purpose because the transformation of intermediates **4a** to ester **5a** was low yielding in the presence of this additive. Therefore, HFIP was used for the first step given the good conversion of substrate **3a** to the mixture of compounds **4a** and **5a** using this additive (Table 1, entry 8). After complete conversion of the starting material **3** at the first stage (equal to 2.2 F/mol of passed charge), acetic acid was added, and the electrolysis was continued for additional 4.0 F/mol of passed charge to obtain products **5**. This procedure led to moderate yields of esters **5a,c,d** from *O*-furfuryl ethylene glycols **3a,c,d**. Gratifyingly, this approach was more productive in the case of synthesis of esters **5h–m** containing protected amine functionality from *O*-furfuryl amino alcohols **3h–m**. It should be noted that ester **5k** synthesis was successfully performed on 0.9 g scale.

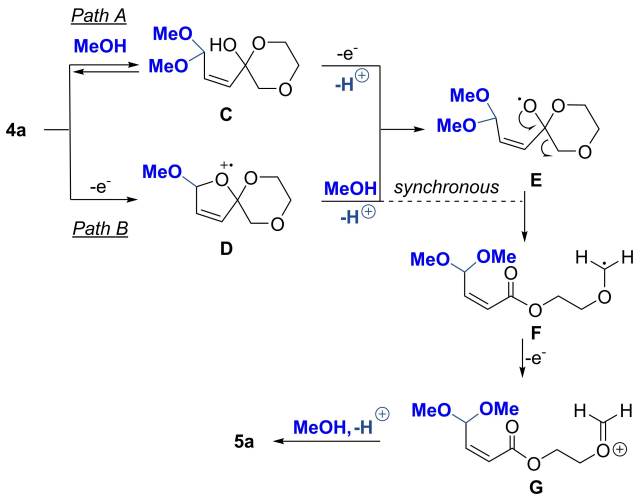
Mechanisms of electrochemical bis-alkoxylation of furan and (methoxy) anisole derivatives have been proposed previously depending on the reaction conditions.[6a,10] For the oxidative fragmentation of spirocycle **4a** to ester **5a** two possible pathways are provided in Scheme 5. Path A involves reversible S_N type methanolysis of the acetal in the dihydrofuran part of spirocycle **4a**, leading to intermediate **C**. Electrochemical oxidation of the hemi-acetal would give the *O*-centered radical **E** which fragments to α-oxy-stabilized *C*-centered radical **F**. Further oxidation of intermediate **F** would give oxonium ion **G** which reacts with methanol giving ester **5a**. The alternative path B starts with electrochemical activation of acetal group in spirocycle **4a** to give radical cation **D** after which the ring opens by methanolysis, leading to *O*-centered radical **E**. It cannot be excluded that methanolysis of activated acetal **D** and fragmentation occurs in a simultaneous fashion leading directly to intermediate **F.**



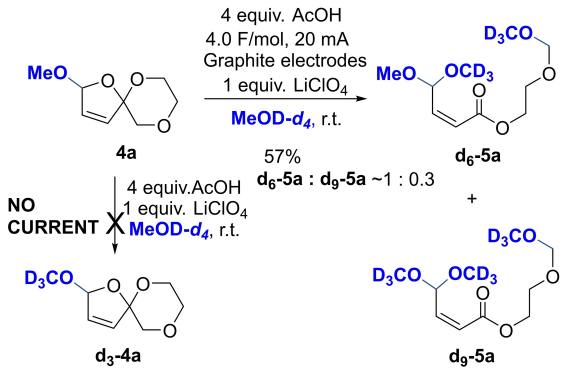
Scheme 3. Transformation of alcohol **3i** to spirocycle **4i** and its fragmentation to ester **5i**.



Scheme 4. One-pot synthesis of esters **5** from alcohols **3**.



Scheme 5. Proposed mechanistic pathways for ester **5 a** formation from spirocycle **4 a**.



Scheme 6. Deuterium labelling experiments supporting path B of ester **5 a** formation mechanism.

To establish if path A is operational, spirocycle **4 a** was subjected to the reaction conditions with no current passing through the reaction mixture and using deuterated methanol as the reaction solvent (Scheme 6). In this case, no deuterium incorporation was observed by ^{1}H-NMR even after 24 hours. However, when the current was passed through the reaction mixture, incorporation of deuterated methanol took place, forming a mixture of the products ***d*$_6$-5 a** and ***d*$_9$-5 a** (ratio 1 : 0.3, detected by ^{1}H-NMR). These results clearly indicated the necessity of electrochemical activation for the methanolysis of spirocycle **4 a** and supported path B of the product **5 a** formation mechanism.

Conclusion

In summary, we have demonstrated an extended application of Torii-type ester electrosynthesis from biomass-derived furan conjugates with glycols and amino alcohols. The ester synthesis from furanoics can be done in two steps or by using one-pot protocol giving multifunctional building blocks and tailored monomers for polymerization. Notably, the reactions can be performed using undivided cell commercial electrochemical set-up using inexpensive graphite electrodes.

Demonstration of the application for the reaction products is planned as the next step of our research work.

Experimental Section

Optimized conditions for spirocycle formation: Substrate (1.0 equiv.), $TBABF_4$ (1.0 equiv.) and PPTS (1.0 equiv.) were transferred to an undivided cell (10 mL) and dissolved in freshly distilled MeOH (7 mL). Graphite electrodes were fitted to the cell and electrolysis was performed in constant current (30 mA) conditions until 2.5 F/mol of charge were passed through the cell. Afterwards the solvent was evaporated, and the product was purified using column chromatography.

Optimized conditions for α,β-unsaturated ester formation: Substrate (1.0 equiv.) and $LiClO_4$ (1.0 equiv.) were transferred to an undivided cell (10 mL) and dissolved in freshly distilled MeOH (7 mL). AcOH (4.0 equiv.) was added. Graphite electrodes were fitted to the cell and electrolysis was performed in constant current (20–30 mA) conditions until 4.0 F/mol of charge were passed through the cell. After electrolysis was done, TEA (4.0 equiv.) was added, and the reaction mixture was filtered through a silica plug. The solvent was evaporated, and product was purified using column chromatography.

Optimized conditions for one-pot transformation of alcohols to α,β-unsaturated esters: Substrate (1.0 equiv.) and $LiClO_4$ (1.0 equiv.) were transferred to an undivided cell (10 mL) and dissolved in freshly distilled MeOH (7 mL). HFIP (20.0 equiv.) was added. Graphite electrodes were fitted to the cell and electrolysis was performed using constant current (20–30 mA) conditions until 2.2 F/mol of charge were passed through the cell. Then AcOH (4.0 equiv.) was added, and electrolysis was continued for another 4.0 F/mol. After electrolysis was done, TEA (4.0 equiv.) was added, and the reaction mixture was filtered through a silica plug. The solvent was evaporated, and the product was purified using column chromatography.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Anodic oxidation · Biomass · Electrochemistry · Furan · α,β-Unsaturated ester

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