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Electrochemical reduction of diheteroaryl-1,2-diketones in the presence of carbonimidoyl dichlorides. First synthesis of 2-arylimino-4,5-di-2-furyl-1,3-dioxoles and (*E*)-1,2-di-2-furylvinylene bis(*N*-arylchloroformimidates)

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Abstract—Selective cathodic reductions of 2,2′-furil in an aprotic medium, under constant potential, in the presence of equimolecular amounts of *N*-arylcarbonimidoyl dichlorides provide previously unknown 2-arylimino-4,5-di-2-furyl-1,3-dioxoles in high yields. These compounds were formed accompanied by minor products which were identified as (*E*)-1,2-di-2-furylvinylene bis(*N*-arylchloroformimidates), a new class of compound. Similar reductions were applied to 2,2′-pyridil, 2,2′-thenil and bis(pyrrol-2-yl)-1,2-ethanedione. However, arylisocyanides were quantitatively generated by mediated electroreduction of arylcarbonimidoyl dichlorides. © 2002 Elsevier Science Ltd. All rights reserved.

Carbonimidoyl dichlorides are inexpensive and easily available reagents[1] in which we recently found an optimal conjunction of chemical and electrochemical properties, which can be exploited in organic electrosynthesis. Thus, carbonimidoyl dichlorides can be quantitatively converted to the corresponding isocyanides by direct cathodic reduction,[2a,b] whereas under the appropriate electrode potential they can also be used as non-electroactive dielectrophilic agents to react with cathodically electrogenerated nucleophilic species. Intermediates originated from benzils and benzil monoanils can be geminally captured in this manner to form the corresponding five-membered heterocycles in high yields.[2c] Given the high potential of this synthetic methodology we attempted the preparation of hitherto unknown 2-arylimino-4,5-diheteroaryl-1,3-dioxoles by cathodic iminocarbonylation of diheteroaryl-1,2-diketones, as is shown in Scheme 1. The chemistry concerning 1,3-dioxoles has been well studied from many points of view. However, the synthesis and properties of 2-imino-1,3-dioxoles remain little known due to previous synthetic difficulties.[3]

Cathodic reductions of 2,2-furil **1** under constant potential were carried out in the presence of carbonimidoyl dichlorides **2**. The electricity consumption was 2 F/mol in all cases. The main reaction products were isolated and identified as 2-arylimino-4,5-di-2-furyl-1,3-dioxoles **3**. These compounds were found accompanied by minor products, which could be isolated and identified as (*E*)-1,2-di-2-furylvinylene bis(*N*-arylchloroformimidates) **4**. The molecular structure of **4f** was determined by X-ray crystallography.[4] As far as we know there are no precedents for either family of compounds **3** or **4**.

Similar reductions were also applied to other representative diheteroaryl-1,2-diketones such as 2,2′-thenil **5g**, bis(pyrrol-2-yl)-1,2-ethanedione **5h** and 2,2′-pyridil **5i**, which were reduced in the presence of phenylcarbonimidoyl dichloride **2a**. However, it was observed that these electrolyses promoted a quantitative generation of phenylisocyanide **6a** instead of the expected heterocyclic compounds. This occurred in spite of the preparative reductions being carried out at a far less negative potential [(**5g**, −0.95); (**5h**, −1.10); (**5i**, −0.80) V versus SCE] than that necessary to generate phenyl isocyanide (−1.80 V versus SCE) by direct electroreduction of phenylcarbonimidoyl dichloride **2a** when a diketone **5** is not present in the catholyte.[2b] The dichloride **2f** was similarly converted to the corresponding isocya-

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Keywords: electrosynthesis; 1,2-diketones; carbonimidoyl dichlorides; dioxoles; formimidates; isocyanides.

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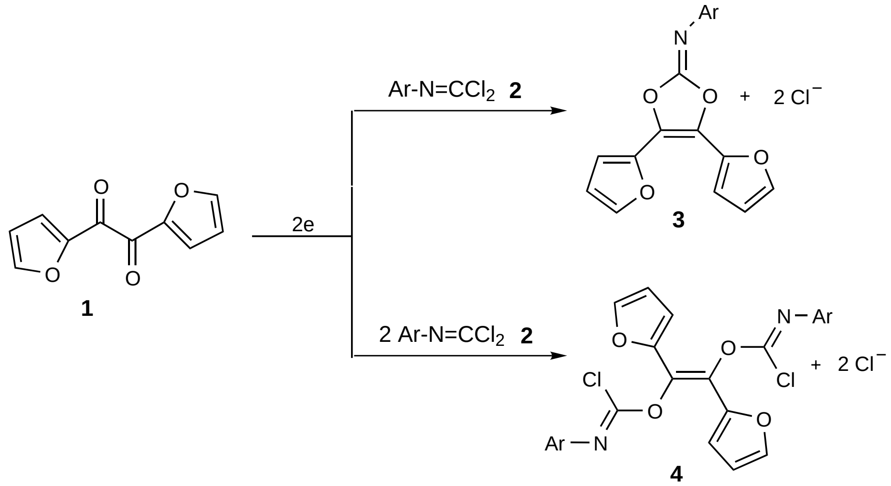
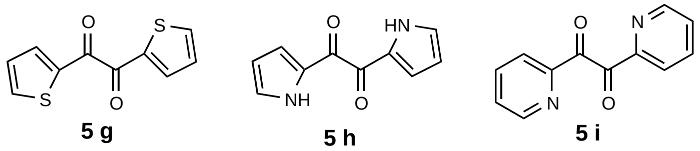


	Ar	**3** (yield %)	**4** (yield %)
a	C_6H_5	74	8
b	$4\text{-}ClC_6H_4$	76	12
c	$2,4\text{-}Cl_2C_6H_3$	73	11
d	$4\text{-}NCC_6H_4$	73	11
e	$4\text{-}BrC_6H_4$	74	13
f	$2\text{-}Cl\text{-}4\text{-}CH_3C_6H_3$	70	10

$$\underset{\mathbf{2}}{\text{Ar-N=CCl}_2} \xrightarrow{\text{2e, }\mathbf{5}} \underset{\mathbf{6}}{\text{Ar-N=C}} + 2\,\text{Cl}^-$$



Scheme 1.

nide **6f**. It should be noted that this peculiar indirect electroactivity has high potentiality in providing a wider scope to our previously reported method for the electrogeneration of isocyanides.[2a,b]

The formation of products **3** can be explained on the basis of electrogeneration of two nucleophilic centers that are geminally captured by non-electroactive dielectrophilic agents present in the catholyte solutions, whereas the formation of products **4** can be similarly justified, but with the participation of two independent dielectrophilic molecules on account of configurational reasons. Of particular interest are the previously reported examples of electrocyclizations of diaryl-1,2-diketones, benzil monoanil and benzil dianil by reduction in the presence of ditosylates. These processes enable the synthesis of unsaturated crown ethers.[5]

Electroreductions of benzil and other 1,2-diketones have been the subject of numerous research papers.[6,7] It has been found that in aprotic solvents these compounds are reduced in two one-electron steps to give the corresponding semidione radical anions and dianions, respectively.[7a,e–g,m] The properties of these reactive species and their synthetic usefulness has been the subject of considerable study. Semidione radical anions can provide the corresponding dianions by disproportion, whereas such dianions can comproportionate with neutral diketone molecules to yield semidione radical anions.[6,7e,8] Nucleophilic as well as reducing activities have been postulated for both types of reactive intermediates.[5,7e,h,j,8a,9,10] Owing to stronger chelation, [7f,8a] of *Z* semidione radical anions with certain metal cations (e.g. Li^+) than that of *E* isomers, priority towards the formation of *Z* enediol derivatives in the selective electroreductions of 1,2-diketones in the presence of electrophilic reagents has been frequently observed. The great interest of the electrogeneration of oxidizing or reducing species to be used in solution to carry out catalytic redox processes should be noted.[11]

Given the above, disparity in the reductions of diketones **1** and **5** can tentatively[12] be explained by considering that the behavior (either nucleophilic or reducing) of the electrogenerated species shows a remarkable dependence on the heteroaryl groups supported by the oxygenated carbon atoms. Thus, furil **1** provides nucleophilic intermediates which undergo electrophilic trapping, whereas those intermediates generated from diketones **5** show a dramatic change of activity into electron transfer agents. Therefore, it is understandable that a less efficient stabilization of the negative charge supported by a electrogenerated intermediate could enhance a reducing character. Hence, it can be presumed that furyl groups are actually providing a better stabilization over the electron excess of such intermediates than the other heteroaryl substituents (**5g**–**i**). The acidity[13] of furan-2-carboxylic acid ($pK_a = 3.15$) is consistently higher than both thiophen-2-carboxylic acid ($pK_a = 3.5$) and pirrol-2-carboxylic acid ($pK_a = 4.4$).

To conclude, it has been established that cathodic reductions of difuryl-1,2-diketones in the presence of carbonimidoyl dichlorides have a specific use for preparing previously unattainable 2-arylimino-4,5-di-2-furyl-1,3-dioxoles and (*E*)-1,2-di-2-furylvinylene bis(*N*-arylchloroformimidates). Also of significance is the discovered ability of diketones **5** to act as electron transfer agents in order to permit the electrochemical generation of isocyanides by indirect reduction of carbonimidoyl dichlorides under a relatively low cathodic potential.

Experimental

Products **3** and **4** were prepared by electrolysis under nitrogen atmosphere at a constant cathodic potential in a concentric cylindrical cell with two compartments separated by a circular glass frit (medium) diaphragm. A mercury pool (diameter 5 cm) was used as the cathode and a platinum plate as the anode. The catholyte was magnetically stirred. The temperature was kept at approximately 18°C by external cooling. The reductions were carried out in DMF–$LiClO_4$, 0.2 M. Approximately 35 and 15 mL of this solution were placed in the cathodic and the anodic compartments, respectively. To prevent accumulation of electrogenerated acid in the anode compartment, anhydrous sodium carbonate (3 g) was placed in this compartment. Solutions of **1** (5 mmol) and carbonimidoyl dichlorides **2** (5 mmol) were electrolyzed under the following cathodic potentials: −0.80 V versus SCE (entries **b**, **c**, **d**); −0.95 V (entries **a**, **f**); −1.05 V (entry **e**). The electricity consumption was 2 F/mol for all cases. All electrolysis products were isolated by dropping the catholyte solution into cold brine (200 mL) and filtering or extracting the mixture with ether. The ether layers were washed with cold water and dried on anhydrous magnesium sulfate. A solid mixture of crude products **3** and **4** was obtained by removing ether under reduced pressure. These were then isolated in a high purity state by fractional crystallization from acetonitrile. Crystallization of products **4** occurred at room temperature, whereas products **3** were obtained by crystallization at−10°C and recrystallization from acetonitrile or petroleum ether. Compound **3a** (pet. ether) mp 125–127°C; **4a** (acetonitrile) mp 173–175°C; **3b** (acetonitrile) mp 138–140°C; **4b** (acetonitrile) mp 211–213°C; **3c** (acetonitrile) mp 132–134°C; **4c** (acetonitrile) mp 193–195°C; **3d** (pet. ether) mp 135°C; **4d** (acetonitrile) mp 225–227°C; **3e** (acetonitrile) mp 139–141°C; **4e** (acetonitrile) mp 238–240°C; **3f** (acetonitrile) mp 118–120°C; **4f** (acetonitrile) mp 174–176°C. All compounds gave satisfactory IR, ^1H, ^{13}C NMR, mass spectra and elemental analyses.

Acknowledgements

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