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# Electrochemical reduction of monothiobenzils in the presence of aroyl chlorides. First synthesis of (Z)-α-benzoyloxy-β-benzoylthiostilbenes

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**Abstract**—The first method for the synthesis of the title compounds has been established involving a stereoselective electrochemical diacylation process. The cathodic reductions of monothiobenzils in an aprotic medium, under constant potential, in the presence of twofold molecular amounts of aroyl chlorides provide previously unknown (Z)-α-benzoyloxy-β-benzoythiostilbenes in high to quantitative yields.

Over the years the cathodic behaviour of diaryl-1,2-diketones has been the object of considerable attention. Preparative cathodic reductions of benzils in protic media lead to benzoins.[1] Overall these reactions correspond to two-electron, two-proton processes, with formation of stilbenediols, which tautomerise to the corresponding benzoins. From a synthetic point of view, however, the cathodic reductions of carbonyl compounds in aprotic media carried out in the presence of electrophilic reagents have a higher interest since the attack of electrogenerated intermediates on the electrophilic reagents may take place instead of simple protonation.[2] Dialkylation,[3] diacylation[4] and iminocarbonylation[5] of benzils and some other related compounds have been successfully promoted in this way.

Monothiobenzils[6] **1** are inexpensive and easily available compounds[6a,b] whose chemistry has scarcely been investigated. The most peculiar chemical feature of these compounds is a surprising ability to undergo reversible polymerisation–depolymerisation processes.[6c,d] It has been proved that monothiobenzil in solution for one and half hours shows an intensive blue colour, which corresponds to a full monomeric state, whereas the complete formation of an emerald green glassy polymer takes place when the solvent is fully removed. From a survey of the literature it is apparent that only a few papers on monothiobenzil chemistry have been reported. The majority of these have been mainly focused in cycloaddition reactions.[6a,b,e,f,g] This is perhaps because the sulfur atom is commonly retained in the formed heterocyclic products. In ionic reactions, however, monothiobenzils as thiones[7] in general exhibit a remarkable proclivity to undergo desulfuration to yield either benzils or the same products as those expected when starting from benzils, for example, in ethanolic solution, monothiobenzil is slowly converted to benzil with evolution of hydrogen sulfide whereas the treatment of monothiobenzil with hydroxylamine leads to benzil dioxime.[6h]

Given the above we are working on a project focused on expanding the range of sulfurated derivatives available from monomeric monothiobenzils on the basis of the peculiar mildness of the electrochemical reactions. As an initial result of this project we herein report the first synthesis of (Z)-α-benzoyloxy-β-benzoylthiostilbenes via cathodic reduction of monothiobenzils in the presence of aroyl chlorides (Scheme 1).

Cathodic reductions of depolymerised monothiobenzils **1** under constant potential were carried out in the presence of aroyl chlorides. The electricity consumption was 2 F/mol in all cases. Single electrolysis products

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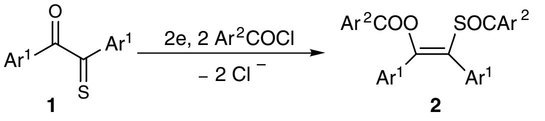

| | $Ar^1$ | $Ar^2$ | mp °C | yield % |
|---|---|---|---|---|
| **2a** | $C_6H_5$ | $4\text{-}CH_3C_6H_4$ | 129-130 | 78 |
| **2b** | $4\text{-}CH_3OC_6H_4$ | $C_6H_5$ | 150-153 | 80 |
| **2c** | $4\text{-}CH_3C_6H_4$ | $C_6H_5$ | 159-161 | 88 |
| **2d** | $4\text{-}CH_3C_6H_4$ | $4\text{-}ClC_6H_4$ | 154-156 | 94 |
| **2e** | $4\text{-}ClC_6H_4$ | $4\text{-}CH_3C_6H_4$ | 112-114 | 76 |

**Scheme 1.**

were formed, which were isolated and, after applying the usual spectroscopic techniques and elemental analysis, were identified as (Z)-α-benzoyloxy-β-benzoylthiostilbenes **2**. Yields ranged from high to quantitative. The molecular structure of product **2c** was determined by X-ray crystallography.[8] As far as we know there are no precedents for this family of compounds.

It should be noted that electroreductions of 1,2-diketones show priority towards the formation of *Z* enediol derivatives. This fact seems to be attributable to a stronger chelation[9] of *Z* semidione radical anions with certain metal cations (e.g., $Li^+$) than that of *E* isomers. Therefore, similar reasons can be tentatively[10] postulated to explain the stereoselective formation of products **2**.

In conclusion, an effective method for the stereoselective synthesis of the previously unattainable family of compounds **2** is reported. This is the first example of electroorganic synthesis from monothiobenzils. The retention of the sulfur atom in the electrolysis products appears to be specially significant. In view of the wide range of nonelectroactive electrophilic reagents available this report points towards a promising general procedure for the preparation of a diversity of sulfurated monothiobenzil derivatives.

## 1. Experimental

Products **2** were prepared by electrolysis under nitrogen atmosphere 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 dry acetone[11]-$LiClO_4$, 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 anodic compartment, anhydrous sodium carbonate (3 g) was placed in this compartment. All the solutions of compounds **1** (5 mmol) and aroyl chlorides (10 mmol) were electrolysed under the same cathodic potential (−1.00 V vs SCE).[12] The electricity consumption was 2 F/mol for all cases. The reaction products were isolated by dripping the catholyte solution into cold water (200 mL) and filtering or extracting the mixture with ether. The ether layers were washed with cold water and dried on anhydrous magnesium sulfate. Crude products were obtained by removing ether under reduced pressure. These were then isolated in a high purity state by crystallisation from methanol. All compounds gave satisfactory IR, $^1H$ NMR, $^{13}C$ NMR, mass spectra and elemental analyses.

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11. This low-cost supporting electrolyte-solvent system was previously used by us in studying electrochemical reductions of acyl chlorides and diaryl-1,2-diketones. See for example: Refs. 4b and 4c.
12. Application of this potential provided reasonably short preparative electrolyses in all cases. The duration ranged from 2.5 to 3.0 h. The average current intensity was 250 mA at the beginning and 10 mA at the end.