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Reaction of 3,3′-bis(2-phenyl-5,5-dimethyl-4-oxopyrrolinylidene) 1,1′-dioxide with the methoxide anion

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*Electrochemical reduction of 3,3′-bis(2-phenyl-5,5-dimethyl-4-oxopyrrolinylidene) 1,1′-dioxide (**1**) in MeCN:MeOH mixtures.*

Electrochemical reduction of **1** in MeCN[1] as well as in MeCN:MeOH mixture with low content of MeOH is an EE process, which is characterized by two well separated one electron and diffusion controlled reversible peaks [Figure S1(*a*)] corresponding with the formation of radical anion and dianion of **1**, respectively within potential sweep region –1.4<E<0.5 V (*vs*. s.c.e). Second peak (2C)

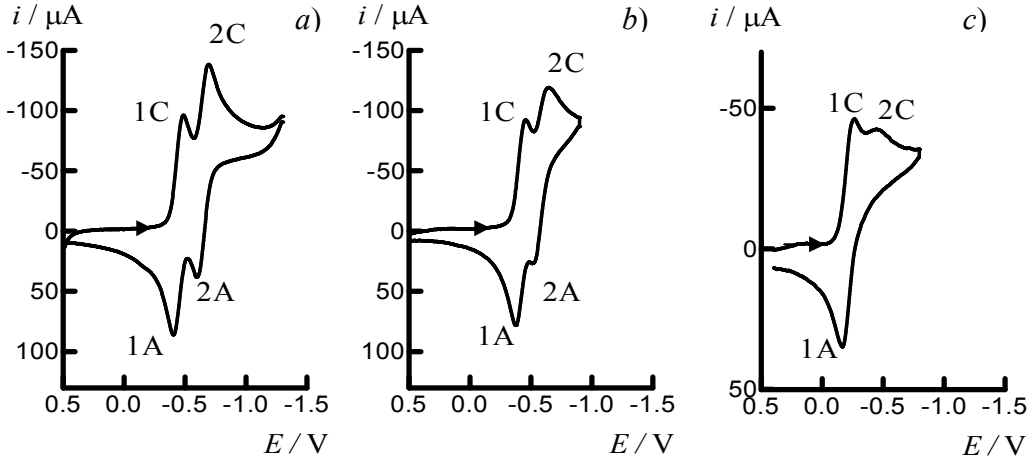

Figure S1 CV of **1** in MeCN:MeOH mixtures (*a, b*) and MeOH (*c*) within potential sweep regions: *a*: –1.3<E<0.5 V, *b*: –0.8<E< 0.5 V, *c*: –0.8<E< 0.4 V at potential sweep rate 0.1 V s^{-1}. Molar fractions of MeOH are the following: 0.048 (*a*), 0.093 (*b*), 1.0 (*c*).

becomes irreversible with the increase in MeOH content [Figure S1(*b*)], and anodic peak 2A is not observed in MeOH [Figure S1(*c*)]. Thus, peak 2C [Figure S1(*a-c*)] corresponds with the formation of the dianion of **1**, which is unstable in MeOH.

*Cyclic voltamogramm of the reaction mixture of **1** after 30 min when K_2CO_3:**1** system was used as a source of MeO^-.*

When K_2CO_3:**1** system was used as a source of MeO^- *in situ* the reaction was completed during 30 min. Cyclic voltamogramm of the reaction mixture is characterized by the only peak 3A–3C which is one-electron and diffusion controlled (Figure S2).

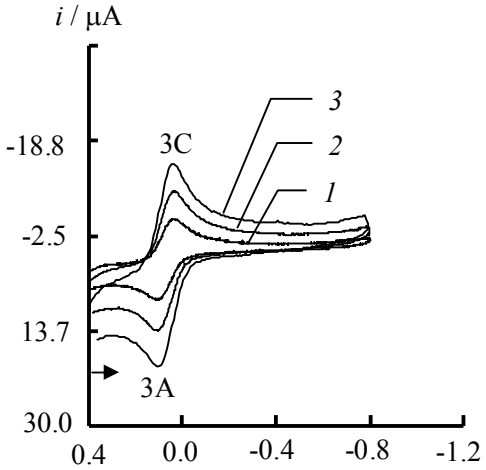

Figure S2 CV of **1** ($7 \cdot 10^{-4}$ M) of the reaction mixture K_2CO_3:**1** in MeOH within potential sweep range $-0.8<E<0.4$ V after 30 min of reaction [ν=0.1 (*1*), 0.3 (*2*), 0.7 (*3*) V s^{-1}].

*Electrochemical reduction of **1** in MeCN with small admixture of MeOH.*

Electrochemical reduction of **1** in MeCN with the addition of MeOH (MeOH:**1**=50:1) mixture is an EE process, which is characterized by two well separated one electron and diffusion controlled reversible peaks (1C, 2C) corresponding to the formation of radical anion and dianion, respectively (Figure S3) within potential sweep region –1.2<E<0.0 V (*vs*. s.c.e). Extension of the potential sweep

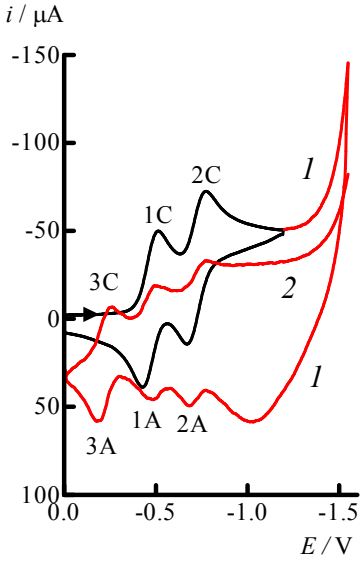

Figure S3 CV of **1** in MeCN with minor content of MeOH (MeOH:**1**=50:1) mixture within potential sweep regions –1.2<E<0.0 V (black curve) and –1.6<E< 0.0 V (red curves) at potential sweep rate 0.1 V s^{-1}. (*1*) first cycle and (*2*) second cycle.

region up to –1.6<*E*<0.4 V led to the appearance of one electron peak 3A at the anodic branch of CV in the first cycle of potential sweep (Figure S3) and redox peaks 3A–3C at both anodic and cathodic branches in the second and subsequent cycles. Peak 3A–3C is associated with the oxidation of anion formed as a result of MeO^- addition to **1.**

Methods and materials.

Solvents were purified using standard procedures. IR spectrum was measured on a Vector 22 spectrophotometer with KBr pellet. UV spectrum was obtained on an HP Agilent 8453 UV-VIS spectrophotometer in MeOH solutions. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer (400 and 100.6 mHz for ^{1}H and ^{13}C, respectively) in CD_3OD solutions using the residual proton signal of CD_3OD as an internal standard.

Reaction of 3,3′-bis(2-phenyl-5,5-dimethyl-4-oxopyrrolinylidene) 1,1′-dioxide with sodium methoxide in MeO.

A solution of **1** (52 mg, 0.13 mmol) and sodium methoxide (7 mg, 0.13 mmol) in MeOH (2 ml) was stirred at room temperature for 30 min. The reaction mixture was distilled off under reduced pressure at room temperature. The crude material was washed with hexane (1 ml) and dried.

MS *m/z*: 457.169 $[M + H^+]^+$, 433.186 $[M - Na^+]^-$.

Synthesis of potassium 4-{1-methoxy-3-phenyl-3-[oxido(propan-2-ylidene)-λ^5-azanyl]-1-oxoprop-2-en-2-yl}-2,2-dimethyl-5-phenyl-3-oxo-2,3-dihydro-1H-pyrrol-1-olate (**2**).

Potassium carbonate (20 mg, 0.14 mmol) was added to the solution of **1** (52 mg, 0.13 mmol) in MeOH (2 ml). The reaction mixture was stirred at room temperature for 30 min. Inorganic salts were filtered off; the filtrate was distilled off under reduced pressure at room temperature. The crude material was washed with hexane (1 ml) to give the reaction product as a yellow solid [57 mg, 93% yield, mp > 50 °C (decomp.)].

^{1}H NMR (400 MHz, CD_3OD, δ_H): 1.21 (s, 6H, 2Me), 1.99 (s, 3H, Me), 2.02 (s, 3H, Me), 3.46 (s, 3H, MeO), 6.99-7.30 (m, 10H, 2Ph). ^{13}C NMR (100.6 MHz, CD_3OD, δ_C): 18.28, 20.89, 142.69,

155.01 (Me_2C=N($\rightarrow$O)-C=), 20.89, 72.22, 191.20 (Me_2C-C=O), 51.87, 159.98 (MeO-C=O), 97.61, 167.90 (-C=C-N), 122.82 (=C-), 127.64, 127.83, 128.35, 128.63, 129.32, 129.61, 135.04 (2Ph). IR (KBr, ν/cm^{-1}): 1594, 1622, 1653, 1668, 1715 (C=C-C=O, C=C-CO_2Me). UV [MeOH, λ/nm (lgε)]: 204 (3.46), 247 (3.37), 401 (2.84). MS *m/z*: 473.157 $[M + H^+]^+$, 433.186 $[M - K^+]^-$.

The structure of **2** was established by means of 1D (^1H and ^{13}C) and 2D (HMBC) NMR spectroscopy. HMBC spectrum of **2** shows the correlation of the methyl protons (δ_H 1.99 and 2.02) with the methyl carbons (δ_C 20.89 and 18.28, respectively), nitrone carbon (δ_C 142.69) and olefinic carbon (δ_C 155.01). Methyl protons (δ_H 1.21) correlate with the methyl carbon (δ_C 20.89), and tertiary carbon (δ_C 72.22) and carbonyl carbon (δ_C 191.20).

References

1. L. A. Shundrin, N. V. Vasilieva, I. G. Irtegova and V. A. Reznikov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2007, 1148 (*Russ. Chem. Bull., Int. Ed*., 2007, **56**, 1273).