ELECTROCATALYTIC ADDITION OF THIOLS TO ACTIVATED OLEFINS

M. E. Niyazymbetov, L. D. Konyushkin,
Z. I. Niyazymbetova, V. P. Litvinov,
and V. A. Petrosyan

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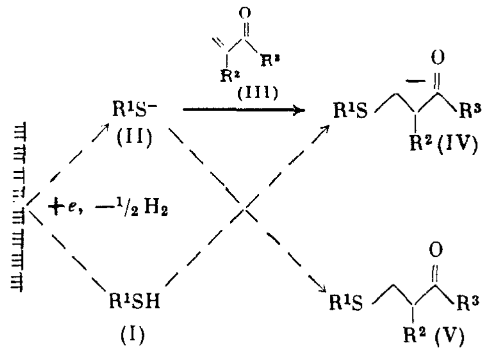
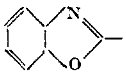
The addition of thiols to activated olefins usually is accomplished in the presence of free radical initiators or bases [1-3]. The product yields are not always high.

In the present work, we established that the electrochemical generation of thiolate anions efficiently initiates the addition of thiols to activated olefins. This is a catalytic reaction described by a scheme entailing the cathodic generation of thiolate anion (II) from thiol (I) and the subsequent nucleophilic addition of (II) to the double bond of an olefin (III). The carbanion formed (IV), which is quite basic, is protonated by the thiol in the solution bulk with the formation of sulfide (V) and thiolate anion (II).



$R^1 = C_8H_{17}$, $C_{12}H_{25}$, $HOCH_2CH_2$, Ph, , .

$R^2 = H$, $R^3 = Me$ (a); $R_2 = H$, $R^3 = OEt$ (b); $R^2 = Me$, $R^3 = OMe$ (c).

We should note that this reaction may be carried out either in a diaphragm or diaphragmless cell using a platinum cathode and magnesium anode. The yields of (V) for R^1 = alkyl, $HOCH_2CH_2$, and Ph are quantitative even after the passage of only 0.0015-0.03 F/mole. For comparison, we note that the electrocatalytic additions of CH-acids such as diethyl malonate and diethyl phenylmalonate to acrylonitrile and ethyl acrylate requires 0.016-0.055 F/mole, while the product yields range from 15 to 77% [4]. The difference in the efficiencies of these reactions is apparently related to the greater nucleophilicity of the thiolate anions in comparison with carbanions. This hypothesis is supported by the finding that the yield of (V) drops (≤70%) upon going from alkylthiolate anions to less nucleophilic heteroarylthiolate anions, while the total conversion of the starting reagents occurs only after passage of 0.15-0.5 F/mole.

In our previous work [5], we demonstrated the feasibility of the electrocatalytic thioalkylation of 2,3-epoxypropyl alkyl sulfides. In this case, the passage of only 0.1 F/mole is required for complete conversion of the starting reagents.

The electrolyses were carried out in 10-50 ml absolute acetonitrile, containing 0.01-0.03 mole (I) and (III) and 0.01-0.1 N Et_4NBr or Bu_4NBr in a galvanostatic regime (i = 0.1-0.5 mA/cm²). The structure of (V) was confirmed by PMR and IR spectroscopy and

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elemental analysis as well as by the correspondence of the physicochemical indices of these products to reported literature values.

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MEDIATED ELECTROCHEMICAL REDUCTION OF 1,1-DICHLOROCYCLOPROPANES

V. V. Yanilkin, N. I. Maksimyuk
E. I. Gritsenko, and Yu. M. Kargin

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The efficiency of electrochemical reactions involving organic electron transfer agents is characterized by the difference in the half-wave potentials of the transfer agent and substrate [1]. We have discovered the unexpected possibility of a multifold acceleration of the reactions of a transfer agent and substrate due to the action of metal ions. Thus, in the case of the electrochemical monodechlorination of substituted 1,1-dichlorocyclopropanes (I)-(III), the effective rate constant (k_{ef}, $M^{-1}sec^{-1}$) of electron transfer from the anthracene radical-anion to the substrate increases in the presence of Ni(II) and Co(II) ions by a factor of from 2 to 16 (see Table 1).

TABLE 1. Electron Transfer Kinetics in DMF at 25°C (the base electrolyte was 0.1 M Bu_4NI and bottom mercury served as the reference electrode)

Substrate*	$k_{ef}\cdot 10^{-2}$	$k_{ef}\cdot 10^{-2}$ [Ni (II)] = 10^{-3} M	$k_{ef}\cdot 10^{-2}$ [Co (II)] = 10^{-3} M
(I)	2,6	43,0	13,8
(II)	1,2	4,3	2,6
(III)	1,3	6,8	6,9

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*(I)) 2-carbomethoxy-2-methyl-1,1-dichlorocyclopropane, (II)) 2,2-diphenyl-1,1-dichlorocyclopropane, (III)) 4-methyl-8,8-dichloro-3,5-dioxabicyclo[5.1.0]octane (anti isomer). $E_{\frac{1}{2}}$ = −2.06 V rel. Hg/I^- (I), −2.20 V (II), −2.14 V (III), −1.44 V (anthracene), −0.60 V ($Ni(BF_4)_2$), −0.74 V ($Co(BF_4)_2$).

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