

Electrochemical Oxidation of α -Bromoketones into Esters

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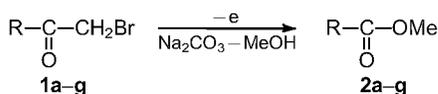
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Electrolysis of α -bromoketones in the presence of Na_2CO_3 in methanol in undivided cell leads to the corresponding methyl esters.

The electrochemical reduction of α -phenacyl bromides at a mercury cathode in DMF or methanol with formation of dimers of different types and bromide ions is a well known process.¹⁻⁴

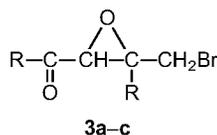
On the other hand, little is known about the electrochemical oxidative transformations of α -bromoketones. To our knowledge, there is only one example of electrochemical oxidation of this type: α -bromoketones were proposed as intermediates in the electrocatalytic variant of the haloform reaction.^{5,6}

In the course of our studies on the electrooxidation of organic compounds in an undivided cell,⁷⁻⁹ we have accomplished the electrochemical oxidative transformation of α -bromoketones in methanol into the corresponding methyl esters (Table 1).



- a** R = Ph
- b** R = 4-ClC₆H₄
- c** R = 4-BrC₆H₄
- d** R = 4-MeC₆H₄
- e** R = 4-PhC₆H₄
- f** R = 4-MeOC₆H₄
- g** R = Bu^t

In some cases a small amount of condensed dimeric compound **3a-c** was also identified in the reaction mixture:

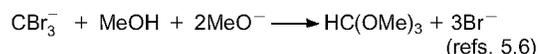
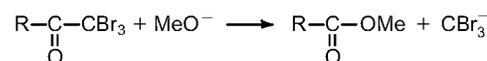
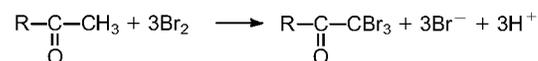
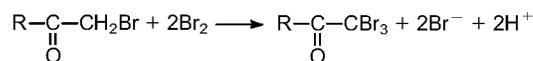
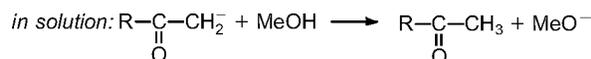
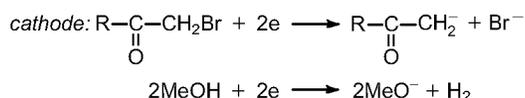


- a** R = Ph
- b** R = 4-ClC₆H₄
- c** R = 4-BrC₆H₄

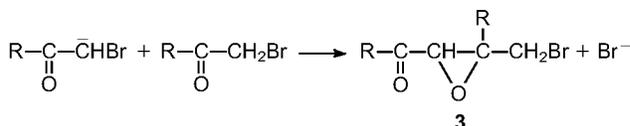
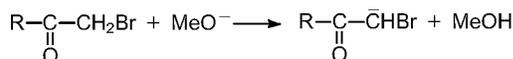
Sodium carbonate is the optimum electrolyte for this process. Its replacement for sodium acetate resulted in formation of a complex mixture of organic compounds. The optimum substrate:electrolyte ratio was found to be 2.5 : 1.

Decreasing the quantity of the electricity passed in the case of **1a** to 1.2 F mol⁻¹ resulted in 84% conversion of **1a** and the formation of PhC(O)Me (36%), **2a** (18%), **3a** (16%) and PhC(O)CHBr₂ (3%).

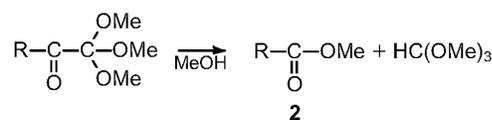
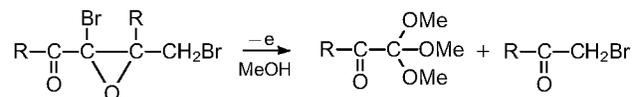
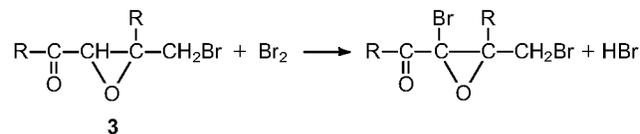
The results obtained, as well as direct observation of the voltage decrease during the process from 20 to 6.5 V and simultaneous dissolution of the electrolyte, allow us to suggest the following main reaction scheme.



Beside all these reactions, in which a catalytic amount of bromide ion is sufficient for transformation of all the RC(O)CH₂Br and RC(O)CH₃ into RC(O)OMe,^{5,6} one more condensation reaction takes place in solution:



Further transformation of the condensed compound **3** under electrolysis conditions also leads to ester **2** by the following general scheme:



Thus the electrooxidation of **3a** (R = Ph) in the presence of 4 mmol of NaBr under the conditions similar to those of electrolysis of α -bromoketones **1a-g** resulted in formation of **2a** in 57% yield.

Table 1 Electrochemical oxidation of α -bromoketones in methanol. ^a

Substrate	R	Products, yields (%)
1a	Ph	2a , 75; 3a , 5
1b	4-ClC ₆ H ₄	2b , 62; 3b , 10
1c	4-BrC ₆ H ₄	2c , 65; 3c , 8
1d	4-MeC ₆ H ₄	2d , 80
1e	4-PhC ₆ H ₄	2e , 83
1f	4-MeOC ₆ H ₄	2f , 86
1g	Bu ^t	2g , 84

^a10 mmol **1a-g**, 4 mmol Na₂CO₃, Fe cathode, Pt anode, 6 Fmol⁻¹ electricity passed, current density 150 mA cm⁻², 40 °C.

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