ELECTROCHEMICAL OXIDATION OF 1,3-DIKETONES IN THE PRESENCE OF HYDROHALIC ACID SALTS

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In the presence of a mediator (sodium iodide) acetylacetone dimerizes with the formation of 3,4-diacetylhexane-2,5-dione, with a yield up to 90%. Salts of 2-halosubstituted 1,3-diketones form more highly enolized cyclic 1,3-diketones - 1,3-cyclohexanedione and dimedone under analogous conditions, with a yield up to 90%.

<u>Keywords</u>: electrolysis, electrochemical oxidation, 1,3-diketones, 3,4-diacetylhexane-2,5-dione, sodium salt of 2-halosubstituted 1,3-diketones.

The recombination reactions of radicals that form during anodic oxidation of organic anions are well known [1]. The formation of a dimer in the electrooxidation of the acetyl-acetone anions with yields of 2 and 11% was reported in [2, 3].

It was assumed that a similar process is also possible for cyclic 1,3-diketones [3], but it was later established [4] that the electrooxidation of cyclic 1,3-diketone anions in an aqueous solution of methanol leads only to condensation of the cyclic 1,3-diketones with formaldehyde, which forms in the electrooxidation of the methanol.

At the same time, the best yield of dimers of malonic ester [5] and acetoacetic and benzoylacetic esters [6] were obtained in indirect electrochemical oxidation using salts of hydroiodic acid as mediator.

As further development of our research into the electrochemical oxidation of organic compounds in the presence of mediators we have investigated the electrochemical oxidation of acetylacetone (1), dimedone (2), and 1,3-cyclohexanedione (3) in the presence of salts of hydrohalic acids. The electrochemical oxidation of solutions of 1,3-diketones 1-3 was carried out in a diaphragmless electrolyzer in a direct current regime, varying conditions with the goal of achieving the maximum yield of the dimer in the case of the oxidation of 1 or of achieving maximum conversion of 2 and 3 at the least costs of electricity.

Under these conditions the basic and practically only product of the oxidation of 1 proved to be dimer 4 (Table 1)



As follows from Table 1, the best solvent for dimerization of 1 to 4 is acetone. We obtained a similar result earlier for the electrochemical dimerization of acetoacetic and benzoylacetic esters [5]. The optimum temperature is 0° C, slight higher than for dimerization of acetoacetic ester (-20°C [5]), and the amount of electricity needed to achieve significant conversion of 1, 2.7-3.0 F/mole, is more than two times greater than needed for acetoacetic ester. Based on the literature data [5-7] and our data, the following mechanism is proposed for the electrochemical dimerization of 1:

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No.	Solvent	I, ℃	Amount of electricity, F/mole	Conversion of 1, %	Yield of 4, % on converted 1 ^b		
1 2 3 4 5 6 7 8	Acetone Acetone Acetone Acetonitrile Methanol Acetone Acetone	$ \begin{array}{r} -20 \\ 0 \\ 20 \\ 50 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ $	1.8 1.8 1.8 1.8 1.8 1.8 2.7 3.0	61 65 60 53 56 46 87 93	57 98(64) 68 61 89 76 97 95(88)		

TABLE 1. Electrochemical Oxidation of Acetylacetone 1 in the Presence of NaI^a

^a46 mmoles acetylacetone, 8 mmoles NaI in 20 ml solvent, Fe cathode, Pt anode, current density 220 mA/cm², temperature variations in course of electrolysis $\pm 2^{\circ}$ C. ^bYield of 4 with respect to supplied 1 given in parentheses.

at anode:
$$2I^{-} - 2e \longrightarrow I_{2}$$

at cathode: $2Na^{+} + 2e \longrightarrow 2Na$
or $2(1) + 2Na \longrightarrow 2CH_{3}C - CH - CH_{3} + H_{2} + 2Na^{+}$
or $2(1) + 2e \longrightarrow 2CH_{3}C - CH - CCH_{3} + H_{2}$

in solution:

$$\begin{array}{c} 0 & - & 0 & 0 & 0 \\ CH_3C-CH-CCH_3 + I_2 \rightarrow CH_3CCH_3 + I^- \\ 0 & 0 & 0 & - & 0 & 0 \\ CH_3CCHICCH_3 + CH_3C-CH-CCH_3 \rightarrow CH_3CCH-CHCCH_3 + I^- \\ (A) & (B) & 0 = C & C = 0 \\ CH_3 & CH_3 & CH_3 & (4) \end{array}$$

$$(1)$$

It should be noted that when electrolysis is carried out in acetone in the presence of NaI at 0°C with passage of 1.8 F of electricity per mole of starting compound the dimer is obtained from malonic ester with a 98% yield and from acetoacetic ester with a 77% yield [5], while dimers obtained from acetylacetone with a yield of only 64% (Table 1, No. 2) with respect to supplied C-H acid. Conversion of the substrate under these conditions was 100, 85, and 65% for malonic ester, acetoacetic ester, and acetylacetone, respectively.

In the electrooxidation of 2 and 3 under similar conditions dimers do not form, as occurs in the case of 1, but rather salts of the corresponding halosubstituted 1,3-diketones (Table 2)

 $\begin{array}{c} R \\ R \\ R \\ (2), (3) \\ R = CH_{3}(2), H(3) \\ R = CH_{3}, (2), H(3) \\ R = CH_{3}, X = I \\ R \\ R = CH_{3}, X = I \\ R = CH_{3}, X = I \\ R = CH_{3}, X = I \\ R = CH_{3}, X = Br \\ R = CH_{3}, X = B$

In acetone at 0°C this reaction has a negligible yield, most likely because of the low solubility of 2 under these conditions. At 50°C, as was noted earlier [6], processes of electrochemically induced polycondensation of carbonyl compounds become significant. Doubling the amount of NaI when the reaction is conducted in acetone has practically no effect

Starting compound	Electro- lyte	Solvent	т, °С	Conversion of starting compound, %	Yield of reaction products, % ^b			
2 2 2 2 3 2 2 3 2 2	Nal Nal Nal Nal Nal Nal Nal	Acetone Acetone Acetone Acetone MeCN MeOH	0 20 20 50 20 20 20 20	11 45 47 25 76 52 62	5a, 14 5a, 56 5a, 46 5a, 16 5b, 94 5a, 15d 5a, 78			

TABLE 2. Electrooxidation of Dimedone 2 and 1,3-Cyclohexanedione 3 in the Presence of Sodium Halides^a

^a10 mmoles of 2 or 3, 8 mmoles of electrolyte in 20 ml solvent: supplied 1.4 F electricity per mole of 2 or 3 (1.8 F electricity per mole of electrolyte), Fe cathode, Pt anode, current density 220 mA/cm², temperature variation in course of electrolysis ±2°C. ^bYield on electrolyte supplied in a deficient amount. ^c16 mmoles NaI. ^dUnder electrolysis conditions the sodium salt of dimedone 6 precipitates, with a yield of 45% on supplied 2.

on the conversion of the cyclic 1,3-diketone or yield of the corresponding halosubstituted salt 5. Electrolysis of 2 in methanol leads to the formation of 5a and 5c, depending on the electrolyte used (NaBr is practically insoluble in acetone). In acetonitrile the sodium salt of dimedone 6 was obtained as the basic product - the result of the low solubility of 6, which forms at the cathode, in the solvent.

The formation of 5a-c, and not the dimer tetraketone, as is the case in the reaction of the electrogenerated intermediates (A) and (B) (see the mechanism of the electrooxidation of acetylacetone):



is most likely due both to the increasing steric hindrances to dimerization in the case of cyclic ketones and to the existence in the solution of 2 and 3 and all intermediate formations primarily in enol form. Since the half-wave oxidation potentials of the anions of C-H acids are close to each other (0.83-0.87 V rel. to Ag/AgCl [8]), an increase of the amount of enol form as one moves from malonic ester to acetoacetic ester and then to acetylacetone is most likely responsible for the slowing of the dimerization step and necessitates an increase of the amount of supplied electricity in this series in order to achieve comparable results with regard to conversion of C-H acid and yield of dimer.

EXPERIMENTAL

The ¹H and ¹³C NMR spectra of the solutions of the substances in DMSO-d₆ were recorded on Bruker M-250 (250 MHz), Bruker AM-300 (300 MHz), and Jeol FX-90 (90 MHz) instruments. Chemical shifts are given on the δ scale using TMS as internal standard.

NaI and NaBr of "pure" grade were additionally dried in vacuum. Acetylacetone 1, dimedone 2, and 1,3-cyclohexanedione 3 of "pure" grade were additionally purified prior to use: 1 by distillation, and 2 and 3 by crystallization from acetone.

<u>Electrolysis of 1,3-Diketones 1-3 in the Presence of Hydrohalic Acids.</u> General Technique. The amount of 1,3-diketones 1-3 indicated in Tables 1 or 2, 8 mmoles NaI or NaBr, and 20 ml solvent were put into a diaphragmless cell with Fe cathode and Pt anode (distance between electrodes ~5 mm) and external cooling. The cell was equipped with a mechanical stirrer, thermometer and reflux condenser, and the amount of electricity indicated in Tables 1 and 2 was passed through the cell at a current density of 220 mA/cm². <u>3,4-Diacetylhexane-2,5-dione (4).</u> Crystalline 4 was filtered from the reaction mixture, the filtrate was concentrated by evaporation, extracted with chloroform, re-evaporated, and quantitative determination of the conversion of 1 and amount of 4 in the filtrate was conducted by PMR spectroscopy using, 1,4-dichlorobenzene as internal standard. Compound 4 crystallized from the reaction mixture and the filtrates were combined and washed in succession with ether and acetone, separating the pure 4, mp 192-193°C. Found, %: C 60.34, H 7.01. $C_{10}H_{14}O_4$. Calculated, %: C 60.61, H 7.07. PMR spectrum (CDCl₃) (δ , ppm). 2.0 s (12H), 16.7 s (2H). ¹³C NMR spectrum (CDCl₃) (δ , ppm): 23.5 q (CH₃), 108.1 s (C), 192.7 s (C=O).

<u>2-Iodo-5,5-dimethylcyclohexane-1,3-dione Sodium Salt (5).</u> In the electrolysis of 2 in acetone 5a was filtered from the reaction mixture, the reaction mixture was evaporated, extracted with chloroform, and conversion of 2 was determined by PMR spectroscopy.

In the electrolysis of 2 in acetonitrile a mixture of 5a and 6 was filtered from the reaction mixture in a ratio that was determined by PMR spectroscopy. The filtrate was evaporated, extracted with chloroform, and the conversion of 2 was determined by PMR spectroscopy.

When electrolysis was conducted in methanol the solvent was evaporated and a mixture of unconverted 2 and NaI was extracted with acetone; pure 5a remained in the residue. The amount of unconverted 2 was determined by PMR spectroscopy. 5a, dec. 210°C. Found, %: C 33.12, H 3.53, I 43.82, Na 7.63. $C_8H_{10}O_2$ INa. Calculated, %: C 33.33, H 3.47, I 44.10, Na 7.99. PMR spectrum (δ , ppm): 0.92 s (6H, CH₃), 2.10 s (4H, CH₂). ¹³C NMR spectrum (δ , ppm): 28.4 qu (CH₃), 50.8 t (CH₂), 74.9 s (C-I), 185.7 s (C=O).

<u>2-Bromo-5,5-dimethylcyclohexane-1,3-dione Sodium Salt (5c).</u> When electrolysis of 2 was conducted in methanol in the presence of NaBr, the reaction mixture was evaporated, the unconverted 2 was extracted with acetone, and conversion of 2 was determined by PMR spectros-copy. Pure 5c was recovered by recrystallization from ethanol. 5c, dec. 91°C. Found, %: C 39.59, H 4.27, Br 32.97, Na 9.61. $C_8H_{10}O_2BrNa$. Calculated, %: C 39.83, H 4.14, Br 33.20, Na 9.54. PMR spectrum (δ , ppm): 0.92 s (6H, CH₃), 2.08 s (4H, CH₂). ¹³C NMR spectrum (δ , ppm): 28.5 qu (CH₃), 51.2 t (CH₂), 95.1 s (C-Br), 183.7 s (C=O).

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