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## Electrochemical Synthesis of Keto and Enol Forms of Tetraketones of the Type 3,4-Diaroyl-2,5-hexanedione by Oxidative Dimerization of Aroylacetones

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Tetraketones of the type 3,4-diaroyl-2,5-hexanedione: Ar = C<sub>6</sub>H<sub>5</sub>-, *p*-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-, 3,4-(CH<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>-, *p*-CH<sub>3</sub>O-C<sub>6</sub>H<sub>4</sub>-, *p*-Cl-C<sub>6</sub>H<sub>4</sub>-, *p*-Br-C<sub>6</sub>H<sub>4</sub>- and 2-C<sub>4</sub>H<sub>9</sub>S- were prepared in good yield by oxidative anodic dimerization of aroylacetones. Electrochemical oxidation was carried out at constant current (4–5 A) in cylindrical cell without diaphragm with Pt-gauze anode and Ni-cathode. Depending on the method used (A or B) and depending on the properties of the electrolysed aroylacetones, dimer-products were isolated as stable keto or enol tautomers. Electrolysis in 80% aqueous methanol (Method A) gave keto or enol tautomers, while electrolysis in absolute methanol (Method B) yielded only enol tautomers.

Oxidation potentials of *para*-substituted benzoylacetones were correlated with Hammett's constants.

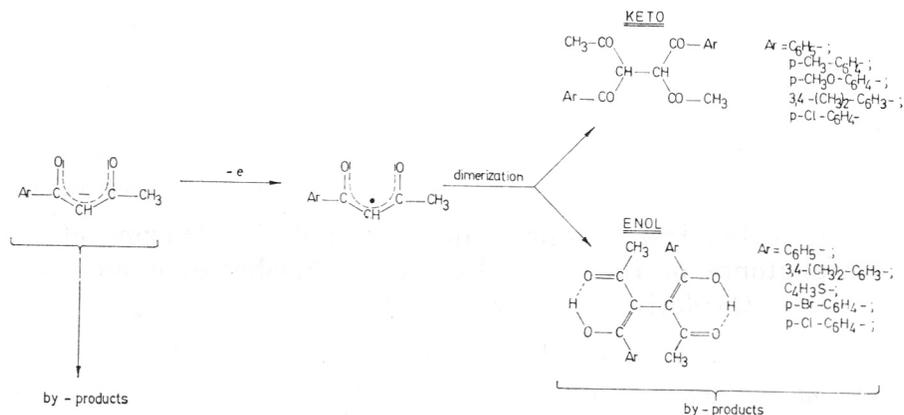
Tetraketones are highly reactive substances and can be used as intermediate products in the synthesis of various aliphatic, aromatic, heterocyclic and polymeric compounds.<sup>1</sup> Therefore recently an increasing interest in the studies of the new methods for their synthesis could be observed.

One of the possible methods for the preparation of tetraketones is electrochemical synthesis in which also the oxidative dimerization of  $\beta$ -diketones takes place. When acetylacetone was electrochemically oxidized, dehydrogen-dimeric products of the electrolysis were obtained<sup>2a,b,c</sup>. However, electrolysis of sodium salts of some  $\beta$ -diketones yields the methylene derivatives<sup>3,4</sup>. Dimerization of other types of enolates has been described<sup>5</sup>.

In the present work dehydrogen-dimers of the type 3,4-diaroyl-2,5-hexanedione were obtained by the electrolysis of aroylacetones.

### RESULTS AND DISCUSSION

During one-electron oxidation of aroylacetone anions at Pt-anode resonance stabilised free radicals can be formed, which then form dimers. This type of dimerization was suggested earlier<sup>6-9</sup>. Besides the expected product of such oxidative dimerizations, a considerable number of by-products is obtained when aroylacetones are electrolysed. This can be represented by the following scheme:



Depending on the method used (method A or B) and depending on the properties of the electrolysed aroylacetone, dehydrogen-dimer products are isolated either as stable keto or as stable enol tautomers.

Both tautomers, *i. e.* keto and enol, were isolated when method A (electrolysis in 80% aqueous methanol) was applied for the oxidation of aroylacetone. It is important to point out that the products of oxidative dimerization of aroylacetones with electron-releasing *para*-substituents are obtained as stable keto tautomers, but enolic tautomers are formed, when electron-withdrawing groups were present. This phenomenon can be explained by the fact that electron-releasing groups increase the stability of the keto form<sup>10a,b</sup> which is in agreement with our experiments.

When the oxidation of aroylacetones was carried out according to the method B (electrolysis in absolute methanol) only enolic tautomers were isolated. This points to the conclusion that absolute methanol exerts an important influence as a reaction medium which favours the formation of enolic tautomer. It is possible that the dimer appears at first as a keto tautomer, and under the influence of the medium is subsequently transformed into the enolic form.

Interconversion of keto and enol forms of 3,4-diaroyl-2,5-hexanedione can be achieved very readily. The enol tautomer was obtained by stirring the keto tautomer 10 to 20 minutes at room temperature in a methanolic solution of sodium hydroxide or sodium ethoxide and then neutralizing with HCl. To convert the enol tautomer into the ketoic, however, it is necessary to reflux the enolic form for 45 minutes in 80% aqueous methanol with an addition of glacial acetic acid.

The linear dependence of the oxidation potential on Hammett's substitutional constants shows that the oxidation mechanism is the same over the whole series of substituted aroylacetones (Fig. 1).

The oxidability of  $\beta$ -diketones is characterized by the anode potential at which the electron transfer occurs from a depolarizer to the electrode. The oxidation occurs at less positive potentials if the  $\pi$ -electron density on  $\beta$ -diketone is higher, and at more positive potentials if the  $\pi$ -electron density is lower<sup>8</sup>.

The oxidability of *para*-substituted benzoylacetones depends on the substituents on the benzene ring. As it is shown in Fig. 1. this dependence is linear. For the substituents *p*-Cl, *p*-Br, and *p*-CH<sub>3</sub>,  $\sigma_p$ -Hammett's values were taken and for the substituent CH<sub>3</sub>O  $\sigma_p^+$ -Brown's value for the electron-releasing *para*-substituent was taken<sup>12</sup>.

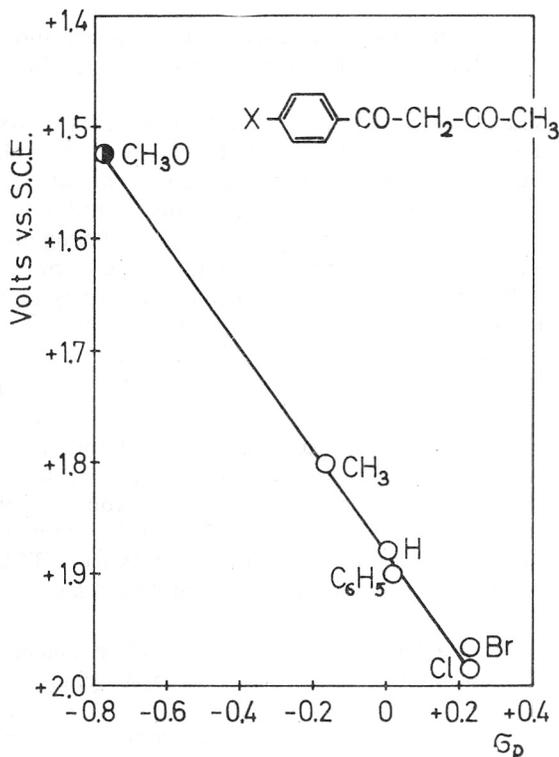


Fig. 1. Relation of oxidation potentials of substituted benzoylacetones to Hammett constants of substituent; ●  $\sigma_p^+$  constant was used

Our results are in good agreement with the well known fact that electron-releasing substituents favour the oxidation and electron-withdrawing substituents hinder the oxidation.

The structure of keto and enol tautomers of 3,4-diaroyl-2,5-hexanedione was proved by the elemental analysis and by infrared, ultraviolet and nmr spectra.

Spectroscopic evidence for the keto and enol forms is conclusive. The spectra of the keto tautomers show the following characteristics: (i) in infrared spectra strong carbonyl absorption bands in 1725–1700 and 1675–1650  $\text{cm}^{-1}$  regions for the acetyl and aroyl groups respectively; (ii) in ultraviolet spectra absorption maximum at 254–268 nm, ( $\log \epsilon_{\text{max}} = 4-5$ ) corresponding to chromophoric system  $\text{Ar}-\text{CO}-\text{CH}=\text{CO}-\text{CH}_3$ <sup>11</sup>; and (iii) in nmr spectra keto- $\text{CH}_3$  resonance at  $\delta = 2.02-2.07$  ppm and  $>\text{CH}=\text{CH}<$  resonance at  $\delta = 5.83-5.87$  ppm.

The spectra of the enol tautomers show the following characteristics: (i) in infrared spectra strong absorption band in the 1610–1530  $\text{cm}^{-1}$  region for chelated carbonyl group; (ii) in ultraviolet spectra absorption maximum at 315–345 nm ( $\log \epsilon_{\text{max}} = 4-5$ ) corresponding to cinnamoyl chromophore<sup>11</sup>, and (iii) in nmr spectra methyl resonance at  $\delta = 2.02-2.08$  ppm and enolic hydroxyl resonance at  $\delta = 16.80-17.53$  ppm.

Although an oxidative dimerization of aroylacetones should in principle lead to a mixture of *d*, *l* and *meso* forms, a nmr spectrum of crude mixture

after electrolysis shows that only one form was present, and we propose that this form is *meso*. Models show that *meso* form is more favoured because of steric effects.

Taking benzoylacetone as a model compound for the oxidation, various physico-chemical conditions which might influence the yield of the dimer product were examined (current density, KOH concentration,  $\beta$ -diketone concentration, temperature)\*. The optimal conditions found were applied to the oxidation of the rest of aroylacetones. Besides the dehydrogen-dimer product, a number of by-products were produced. Using gas chromatographic analysis the following liquid by-products were identified: acetaldehyde, acetone, diacetyl, formic acid, benzaldehyde, methyl benzoate and acetophenone. The conditions of the analysis are similar to those described earlier<sup>9</sup>, and the above mentioned compounds have been identified by the use of analytically pure substances.

We have also examined the hydrolytic influence of the reaction medium on benzoylacetone and on 3,4-dibenzoyl-2,5-hexanedione. In both cases acetic and benzoic acids appear as the products of hydrolysis, while in the case of benzoylacetone additional acetophenone has been found. During 20 min of hydrolysis at room temperature about 10–15% of the dimer product decomposes in the reaction medium giving several substances (TLC). The determination of the structure and the identification of those substances was not the subject of this study.

By-products of the electrochemical oxidation of aroylacetone are produced through heterolytic and homolytic cleavage of benzoylacetone and its dehydrogen-dimer product.

Among the examined factors which are influencing the yield of 3,4-dibenzoyl-2,5-hexanedione, the influence of temperature is very significant. Fig. 2 shows the influence of temperature on the relationship of the hydrolysis and the electrochemical oxidation of benzoylacetone. The ratio of 3,4-dibenzoyl-2,5-hexanedione (one of the products of the oxidative dimerization according to the method A) and acetophenone (the product of the hydrolytic cleavage) is lowered.

The optimal temperature was between 0 and 5 °C, which can be explained by the fact that side reactions are hindered at lower temperatures.

The electrolytic conductivity (1 M KOH) is high enough to permit the electrolysis at relatively high currents (4 to 5 A) which shortens the time for the electrolysis down to 15–30 minutes. By this way the side reactions have been eliminated to a high degree.

As mentioned before, due to the influence of the medium, partial hydrolytic cleavage of benzoylacetone, as well as of dimer products of the electrolysis, occurs. The hydrolysis is faster when the content of water in the reaction medium is higher. When the electrolysis was carried out in 50%, 60%, and 70% aqueous methanol, no dimer product was isolated at all, or it was isolated in insignificant quantities.

By the electrochemical oxidative dimerization of aroylacetones dehydrogen-dimer products were obtained in good yield (15–60%), which means that this

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\* We have examined other solvent-supporting electrolyte systems by electrolyses at controlled potential and at constant current density (MeCN/Et<sub>4</sub>NOH; MeCN/Et<sub>4</sub>NClO<sub>4</sub>; MeOH/NaClO<sub>4</sub>; MeCN/KBr; MeOH/KBr; H<sub>2</sub>O/NaOH), but we did not obtain the expected dimer. The use of divided cell does not affect the yield of product essentially.

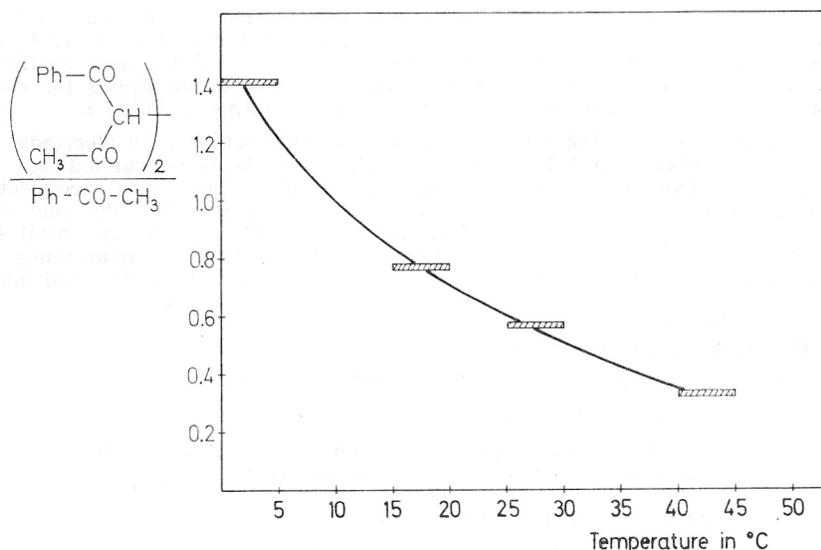


Fig. 2. Influence of temperature on selectivity between the reactions of hydrolysis and electrochemical oxidation of the benzoylacetones

method can be considered suitable for the synthesis of tetraketones of the type 3,4-diaroyl-2,5-hexanedione in either their keto or enolic form.

#### EXPERIMENTAL

*General.* Melting points were determined on a Koffler instrument and are given without correction.

Infrared spectra were recorded on a Perkin-Elmer Infracord 137 instrument. The spectra in the solid phase were determined by incorporating the materials in potassium bromide pellets.

Ultraviolet spectra were recorded on a Perkin-Elmer UV Model 137 instrument.

Nuclear magnetic resonance spectra were recorded on a standard Varian A-60 instrument. Sample temperature was about 30°C. Chemical shifts are reported in  $\delta$  values using TMS as internal standard.

Gas chromatographic analysis was done with the instrument Perkin-Elmer F. 11. on the column Carbowax 20 M on Chromosorb W (60–80 mesh).

Aroylacetones were prepared by standard procedures. Crude products were purified through multiple recrystallization or by redistillation *in vacuo*.

*Apparatus and procedure.* Electrolysis was carried out in a 120 ml flat-bottomed cylindrical cell without diaphragm equipped with Pt-gauze (5 × 7.5 cm) as anode and Ni-foil as cathode. The distance between the electrodes was 0.6 cm and they were fixed by teflon rings. The potential was measured by a tube voltmeter against S.C.E. Electrolyte was stirred with magnetic stirrer and cooled with a mixture of ice and salt in which the cell was placed.

*Method A.* KOH (5.6 g, 0.1 mole) was dissolved in 80% aqueous methanol (100 ml) and the solution was cooled to 0°C. Aroylacetone (0.0125–0.025 mole) was added and electrolysis was carried out at constant current ( $I = 4\text{--}5$  A) during 15 to 30 min (ca. 2 Faraday per mole). The temperature was maintained between 0 and 10°C. Electrolysed and diluted mixture with 250 g of ice was neutralized with acetic acid to pH = 4. After standing for a few hours in a refrigerator the solids were filtered off and recrystallized from alcohol, or solvent was decanted from the above oily residue which was then suspended in cca 10 ml of methanol; crystallized product was filtered off and purified by recrystallization.

*Method B.* KOH (5.6 g, 0.1 mole) was dissolved at room temperature in absolute methanol (100 ml). Aroylacetone (0.020–0.025 mole) was added to the solution which

had been cooled down to 0°C. The electrolysis was carried out at constant current (4–5 A) during 15–20 min (ca. 2 Faraday per mole) at temperature 5–15°C. After the electrolysis and neutralization the product was filtered off and purified by recrystallization from hexane or benzene. The experimental conditions for electrochemical oxidative dimerizations of aroylacetones are shown in Table I.

*Polarization curves.* Polarization curves for the rotating Pt-electrode were recorded on Radelkis OH-102 polarograph. Experiments were carried out in a two-electrode electrolytic cell with a diaphragm. S. C. E. served as reference electrode. Solutions of aroylacetone ( $6.2 \times 10^{-3}$  M) were prepared just before the polarization curves were recorded. Supporting electrolyte was 0.5 M  $\text{CH}_3\text{COONa}$  in glacial acetic acid. The oxidation potentials of various para-substituted benzoylacetones were obtained by extrapolating polarization curves to the value of the residual current.

*Reaction products.*

*3,4-Dibenzoyl-2,5-hexanedione (1):*

IR spectrum:  $\nu = 1730$  vs ( $\text{CH}_3\text{C}=\text{O}$ ) and  $1676$   $\text{cm}^{-1}$  vs (arom.  $\text{C}=\text{O}$ );  
 UV spectrum:  $\lambda_{\text{max}}^{\text{chloroform}} = 254.5$  nm ( $\log \epsilon_{\text{max}} = 4.432$ );  
 NMR spectrum:  $\delta/\text{ppm} = 2.02$  singlet ( $\text{CH}_3\text{C}=\text{O}$ ), 5.87 singlet ( $> \text{CH}-\text{CH} <$ ) and multiplet with center at 7.78 (aromatic).

*3,4-Di-p-toluyyl-2,5-hexanedione (2):*

IR spectrum:  $\nu = 1720$  vs ( $\text{CH}_3\text{C}=\text{O}$ ) and  $1670$   $\text{cm}^{-1}$  vs (arom.  $\text{C}=\text{O}$ );  
 UV spectrum:  $\lambda_{\text{max}}^{\text{ethanol}} = 268$  nm ( $\log \epsilon_{\text{max}} = 4.472$ ) and  
 $\lambda_{\text{max}}^{\text{ethanol}} = 207$  nm ( $\log \epsilon_{\text{max}} = 4.376$ );  
 NMR spectrum:  $\delta/\text{ppm} = 2.06$  singlet ( $\text{CH}_3\text{C}=\text{O}$ ), 2.45 singlet (Ar- $\text{CH}_3$ ), 5.86 singlet ( $> \text{CH}-\text{CH} <$ ) and 7.7 (aromatic quartet)

*Anal.*  $\text{C}_{22}\text{H}_{22}\text{O}_4$  (350.40) calc'd.: C 75.41; H 6.33  
 found: C 75.20; H 6.59

*3,4-di-p-anisoyl-2,5-hexanedione (3):*

IR spectrum:  $\nu = 1720$  vs ( $\text{CH}_3\text{C}=\text{O}$ ) and  $1660$   $\text{cm}^{-1}$  vs (arom.  $\text{C}=\text{O}$ );  
 UV spectrum:  $\lambda_{\text{max}}^{\text{ethanol}} = 280$  nm,  $\lambda_{\text{max}}^{\text{ethanol}} = 224$  nm and  
 $\lambda_{\text{max}}^{\text{ethanol}} = 205$  nm;  
 NMR spectrum:  $\delta/\text{ppm} = 2.08$  singlet ( $\text{CH}_3\text{C}=\text{O}$ ), 3.90 singlet ( $\text{CH}_3\text{O}$ ), 5.85 singlet ( $> \text{CH}-\text{CH} <$ ) and 7.58 (aromatic quartet)

*Anal.*  $\text{C}_{22}\text{H}_{22}\text{O}_6$  (382.40) calc'd.: C 69.10; H 5.80  
 found: C 69.06; H 5.67

*3,4-di-(3,4-xyloyl)-2,5-hexanedione (4):*

IR spectrum:  $\nu = 1725$  vs ( $\text{CH}_3\text{C}=\text{O}$ ) and  $1665$   $\text{cm}^{-1}$  vs (arom.  $\text{C}=\text{O}$ );  
 UV spectrum:  $\lambda_{\text{max}}^{\text{ethanol}} = 266$  nm and  $\lambda_{\text{max}}^{\text{ethanol}} = 207$  nm;  
 NMR spectrum:  $\delta/\text{ppm} = 2.03$  singlet ( $\text{CH}_3\text{C}=\text{O}$ ), 2.31 singlet (Ar- $\text{CH}_3$ ), 5.83 singlet ( $> \text{CH}-\text{CH} <$ ) and multiplet with center at 7.61 (aromatic).

*Anal.*  $\text{C}_{24}\text{H}_{26}\text{O}_4$  (378.48) calc'd.: C 76.16; H 6.93  
 found: C 75.94; H 7.07

*2,3-Diacetyl-1,4-diphenyl-1,3-butadiene-1,4-diol. (5):*

IR spectrum:  $\nu = 1600$   $\text{cm}^{-1}$  vs (chelated carbonyl group);  
 UV spectrum:  $\lambda_{\text{max}}^{\text{chloroform}} = 324$  nm ( $\log \epsilon_{\text{max}} = 4.087$ ) and  
 $\lambda_{\text{max}}^{\text{chloroform}} = 262$  nm ( $\log \epsilon_{\text{max}} = 4.061$ );

TABLE I  
 Reactants and Products in Electrolysis of Aroylacetonates at Various Experimental Conditions

Aroylacetonates Ar	Grams of aroylacetonates	Method used	Current A	Anode potential (measured) vs. S. C. E. V	Percentage yield of product (form)	m. p. °C	Solvent for re- crystallization
C <sub>6</sub> H <sub>5</sub> —	4.05	A	4	1.75—1.90	62 (keto)	178—180 <sup>a</sup>	ethanol
<i>p</i> -CH <sub>3</sub> —C <sub>6</sub> H <sub>4</sub> —	4.4	A	4	1.85—1.95	16.5 (keto)	170—171	ethanol
<i>p</i> -CH <sub>3</sub> O—C <sub>6</sub> H <sub>4</sub> —	4.8	A	4	1.50—1.70	36 (keto)	158—161	ethanol
3,4-(CH <sub>3</sub> ) <sub>2</sub> —C <sub>6</sub> H <sub>3</sub> —	4.76	A	5	1.90—2.00	27 (keto)	157—161	ethanol
C <sub>6</sub> H <sub>5</sub> —	4.05	B	5	—	25 (enol)	144—146	benzene
C <sub>4</sub> H <sub>9</sub> S—	4.2	A and B	4	1.75—1.80	35 (enol)	153—155	ethanol and benzene
<i>p</i> -Br—C <sub>6</sub> H <sub>4</sub> —	3.0	A and B	4	1.65—1.82	15 (enol)	168—170	ethanol and benzene
<i>p</i> -Cl—C <sub>6</sub> H <sub>4</sub> —	4.9	A and B	5	1.70—1.80	30 (enol)	148—150	ethanol
3,4-(CH <sub>3</sub> ) <sub>2</sub> —C <sub>6</sub> H <sub>3</sub> —	4.76	B	5	—	24 (enol)	122—124	benzene

<sup>a</sup> lit.<sup>13</sup> m. p. = 178—180 °C

NMR spectrum:  $\delta/\text{ppm} = 2.02$  singlet ( $\text{CH}_3\text{C}=\text{O}$ ), 7.3 singlet (aromatic) and 17.35 (enolic OH).

*Anal.*  $\text{C}_{20}\text{H}_{18}\text{O}_4$  (322.24) calc'd.: C 74.55; H 5.63  
found: C 74.70; H 5.72

*2,3-Diacetyl-1,4-di(3,4-xylyl)-1,3-butadiene-1,4-diol (9):*

IR spectrum:  $\nu = 1605 \text{ cm}^{-1}$  s (chelated carbonyl group);

$\lambda_{\text{max}}^{\text{chloroform}} = 322 \text{ nm}$  ( $\log \epsilon_{\text{max}} = 4.291$ ) and

UV spectrum:  $\lambda_{\text{max}}^{\text{chloroform}} = 268 \text{ nm}$  ( $\log \epsilon_{\text{max}} = 4.028$ );

NMR spectrum:  $\delta/\text{ppm} = 1.96$  singlet ( $\text{CH}_3\text{C}=\text{O}$ ), 2.19 singlet and 2.24 singlet ( $\text{Ar}-\text{CH}_3$ ), multiplet with center at 7.15 (aromatic) and 17.53 (enolic OH).

*Anal.*  $\text{C}_{24}\text{H}_{26}\text{O}_4$  (378.48) calc'd.: C 76.16; H 6.93  
found: C 76.18; H 6.90

*2,3-Diacetyl-1,4-di(2-thienyl)-1,3-butadiene-1,4-diol (6):*

IR spectrum:  $\nu = 1540 \text{ cm}^{-1}$  s (chelated carbonyl group),

UV spectrum:  $\lambda_{\text{max}}^{\text{ethanol}} = 345 \text{ nm}$  ( $\log \epsilon_{\text{max}} = 4.465$ ).

$\lambda_{\text{max}}^{\text{ethanol}} = 275 \text{ nm}$  ( $\log \epsilon_{\text{max}} = 4.069$ ) and

$\lambda_{\text{max}}^{\text{ethanol}} = 204 \text{ nm}$  ( $\log \epsilon_{\text{max}} = 4.047$ );

NMR spectrum:  $\delta/\text{ppm} = 2.05$  singlet ( $\text{CH}_3\text{C}=\text{O}$ ), 7.0, 7.5 and 7.9 quartets (thienyl) and 16.8 (enolic OH).

*Anal.*  $\text{C}_{18}\text{H}_{14}\text{O}_4\text{S}_2$  (334.41) calc'd.: C 57.46; H 4.22; S 19.77  
found: C 57.19; H 4.21; S 19.41

*2,3-Diacetyl-1,4-bis(p-bromophenyl)-1,3-butadiene-1,4-diol (7):*

IR spectrum:  $\nu = 1600 \text{ cm}^{-1}$  (chelated carbonyl group);

UV spectrum:  $\lambda_{\text{max}}^{\text{ethanol}} = 315 \text{ nm}$  ( $\log \epsilon_{\text{max}} = 4.106$ ),

$\lambda_{\text{max}}^{\text{ethanol}} = 262 \text{ nm}$  ( $\log \epsilon_{\text{max}} = 4.298$ ) and

$\lambda_{\text{max}}^{\text{ethanol}} = 212 \text{ nm}$  ( $\log \epsilon_{\text{max}} = 4.330$ );

NMR spectrum:  $\delta/\text{ppm} = 2.07$  singlet ( $\text{CH}_3\text{C}=\text{O}$ ); 7.35 (aromatic multiplet) and 16.9 (enolic OH).

*Anal.*  $\text{C}_{20}\text{H}_{16}\text{O}_4\text{Br}_2$  (480.16): calc'd.: C 50.05; H 3.33; Br 33.43;  
found: C 49.96; H 3.58; Br 33.05;

*2,3-Diacetyl-1,4-bis(p-chlorophenyl)-1,3-butadiene-1,4-diol (8):*

IR spectrum:  $\nu = 1590 \text{ cm}^{-1}$  (chelated carbonyl group);

UV spectrum:  $\lambda_{\text{max}}^{\text{chloroform}} = 317 \text{ nm}$  ( $\log \epsilon_{\text{max}} = 4.284$ ) nad

$\lambda_{\text{max}}^{\text{chloroform}} = 261 \text{ nm}$  ( $\log \epsilon_{\text{max}} = 4.143$ );

NMR spectrum:  $\delta/\text{ppm} = 2.07$  singlet ( $\text{CH}_3\text{C}=\text{O}$ ), 7.3 singlet (aromatic) and 17.35 (enolic OH).

*Anal.*  $\text{C}_{20}\text{H}_{16}\text{O}_4\text{Cl}_2$  (391.26) calc'd.: C 61.40; H 4.12; Cl 18.12;  
found: C 61.55; H 4.13; Cl 18.09;

*Interconversion of keto and enol forms of tetraketones. 3,4-bis(p-chlorophenyl)-2,5-hexanedione (10).* A suspension of 2,3-diacetyl-1,4-bis(p-chlorophenyl)-1,3-butadiene-1,4-diol (0,195g, 0,0005 mole) in 80% aqueous methanol (15 ml) and some glacial

acetic acid was stirred and heated at reflux temperature during 45 minutes. The crude product 0.176 g (90%) was recrystallized from methanol giving colorless needles, m. p. 167—169 °C;

IR spectrum:  $\nu = 1727$  vs ( $\text{CH}_3\text{C}=\text{O}$ ) and  $1670\text{ cm}^{-1}$  (arom.  $\text{C}=\text{O}$ );

UV spectrum:  $\lambda_{\text{max}}^{\text{ethanol}} = 265\text{ nm}$  and  $\lambda_{\text{max}}^{\text{ethanol}} = 224\text{ nm}$

NMR spectrum:  $\delta/\text{ppm} = 2.02$  singlet ( $\text{CH}_3\text{C}=\text{O}$ ), 5.78 singlet ( $=\text{HC}-\text{CH}=\text{}$ ) and multiplet with center at 7.81 (aromatic).

*Anal.*  $\text{C}_{20}\text{H}_{16}\text{O}_4\text{Cl}_2$  (391.26) calc'd.: C 61.40; H 4.12; Cl 18.12  
found: C 61.69; H 4.34; Cl 18.18

This compound was noticed only in traces when electrolysis of p-chlorobenzoyl-acetone according the method A was carried out.

*3,4-Diacetyl-1,4-diphenyl-1,3-butadiene-1,4-diol.* Procedure a). — Metallic sodium (0.138 g, 0.006 mole) was dissolved in absolute methanol (15 ml) and the solution of sodium ethoxide thus prepared was cooled to room temperature. 3,4-Diphenyl-2,5-hexanedione (0.967 g, 0.003 mole) was added and reaction mixture was stirred during 10 minutes, then poured into 100 g of ice and neutralized with dilute HCl to pH = 4. Crude product (0.87 g, 90%) was filtered off, dried and recrystallized from hexane or benzene. Golden-yellow needles were obtained, m. p. 144—146 °C decomp. (Procedure b). — Sodium hydroxide (0.120 g, 0.003 mole) was dissolved in absolute methanol (10 ml) and 3,4-diphenyl-2,5-hexanedione (0.484 g, 0.0015 mole) was added at room temperature. Reaction mixture was stirred 20 minutes and golden-yellow solution was obtained and poured into 100 g of ice and neutralized with dilute HCl to pH = 4. Crude product (0.412 g, 85%) was filtered off, dried and recrystallized from hexane or benzene. Golden-yellow needles were obtained, m. p. 144—146 °C decomp.

Synthesized 3,4-diacetyl-1,4-diphenyl-1,3-butadiene-1,4-diol by Method B or Procedures a) and b) has the same physical constants and shows the same characteristic bands in the spectra.

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## IZVOD

**Elektrokemijska sinteza keto i enolne forme tetraketona tipa  
3,4-Diaroil-2,5-heksandiona oksidativnom dimerizacijom aroilacetona**

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Sintetizirani su tetraketonni tipa 3,4-diaroil-2,5-heksandiona ( $\text{Ar}=\text{C}_6\text{H}_5-$ ;  $p\text{-CH}_3\text{-C}_6\text{H}_4$ ;  $3,4\text{-(CH}_3)_2\text{-C}_6\text{H}_3-$ ;  $p\text{-Cl-C}_6\text{H}_4-$ ;  $p\text{-CH}_3\text{O-C}_6\text{H}_4-$ ;  $p\text{-Br-C}_6\text{H}_4-$  i  $\text{C}_4\text{H}_9\text{S-}$ ) reakcijom oksidativne anodne dimerizacije aroilacetona. Elektrokemijska oksidacija izvršena je pri konstantnoj struji (4–5 A), u cilindričnoj ćeliji bez dijafragme s Pt-mrežastom anodom i Ni-katodom. Ovisno o metodi elektrolize (A ili B), kao i svojstvima elektroliziranog aroilacetona izolirani su dimerni produkti kao stabilni keto ili enolni tautomeri. Elektrolizom u 80%-tnom vodenom metanolu (Metoda A) dobiveni su keto ili enolni tautomeri tetraketona. Međutim, elektrolizom u apsolutnom metanolu (Metoda B) dobiveni su samo enolni tautomeri.

Oksidacijski potencijali *para*-supstituiranih benzoilacetona korelirani su s Hammettovim konstantama.

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