ELECTROSYNTHESIS OF ORGANIC COMPOUNDS XII
SYNTHESIS OF SOME ARYLACETYLACETONE DERIVATIVES*

M.T. Ismail

Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt

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Electrosynthesis of some arylacetylacetone derivatives was carried out via the anodic oxidation of acetylacetone in absolute methanol containing 0.8 gm atom/e-v sodium metal in the presence of selected aromatic compounds (benzene, toluene, o-xylene, naphthalene and anthracene) on platinum anode under controlled anodic potential value of + 1.1 ± 0.03 V vs SCE at 20°C. The synthesised compounds were 3-phenyl 2,4-pentanedione, 3-(p-tolyl) 2,4-pentanedione, 3-(o-xylyl) 2,4-pentanedione, 3-(α -naphthyl) 2,4-pentanedione and 3-(9-anthryl) 2,4-pentanedione. In addition, a small amount of dimerised and polymerized products was obtained. A suitable mechanism involving the formation of acetylacetone radical intermediates $CH_3\dot{C}OCHCOCH_3$ is suggested.

Also, the potentiostatic studies of the anodic oxidation of acetylacetone were carried out and the anodic oxidation potential was determined.

Electrochemical oxidation of β-diketone was first investigated by Mulliken [1], who reported that the prolonged electrolysis of acetylacetone in 50% aqueous methanol gave a small quantity (2 %) of tetracetylethane. The anodic oxidation of acetylacetone and cyclic B-diketones [2] in aqueous or aquo-alcoholic NaOH (0.1 mol/l) solutions gave a larger yield of tetracetylethane (11%) and bicyclic β-diketones (20-50%). Mechanism of formation of these compounds involves the free radical intermediate species [3-6].

The present work was carried in continuation of our interest in the electrosynthesis of organic compounds [7-10] and that the electrosynthesis of arylacetylacetone derivatives was not reported.

EXPERIMENTAL

Instrumentation

The cell and electrodes are similar to that described earlier [10]. IR spectra and TLC were used in characterizing the products as before[10]. In addition, a column chromatograph of 2 x 150 cm charged with silica gel was used for separation of the products.

Chemicals used

Benzene (Fluka), toluene (Prolabo), o-xylene (Merck), naphthalene (Merck) and antheracene (Merck) were used after further purification using known methods. The purity was checked by boiling point or melting point determination and/or by chromatography.

Authentic samples of 3-phenyl 2,4-pentanedione, 3-(p-tolyl)2,4-pentanedione, 3-(o-xylyl) 2,4-pentanedione, 3-(α naphthyl) 2,4-pentanedione, 3-(9-anthryl) 2,4-pentanedione and diacetylacetone were prepared as described in the literature procedure [2,11-14].

General Procedure

1.84 g of sodium metal was dissolved in absolute methanol (60 ml) and 8 ml acetylacetone was mixed with it and placed in the anode compartment. Benzene (20 ml), or toluene (20 ml), or o-xylene (20 ml), or naphthalene (0.2 mol, 2.56 gm) or anthracene (saturated solution) was mixed with it). The cathode compartment was filled with 30 ml absolute methanol containing 0.4 gm atom sodium metal. Electrolysis was carried out for periods of 56-72 hrs under anodic potential maintained

at +1.1 ± 0.03 V vs SEC at 20°C. The colour of the anode solution gets darker with time but no gas evolution on the surface of the anode was observed. At the end of the electrolysis, excess methanol from the anode mixture was distilled under atmospheric pressure. To the residue, 100 ml H_2O was added and extracted three times with 150 ml ether. The ether extract was washed with H_2O, dried over anhydrous $MgSO_4$ and filtered. The ether filtrate was distilled using rotatory evaporator, under the atmospheric pressure (exp. 1,2,5,6) or under reduced pressure (exp. 3,4). The organic residue was analyzed using thin layer chromatography, column chromatography [silica gel neutral, petroleum ether (100%), petroleum ether - benzene mixture (1:1), benzene (100%), benzene - ether mixture (1:1), ether (100%), ether-methanol mixture (1:1) and methanol (100%) respectively] and Infer-red techniques.

RESULTS AND DISCUSSION

Products

Electrosynthesis of some arylacetylacetone compounds was carried out by the oxidation of acetylacetone in absolute methanol at a Pt anode at a potential of + 1.10 ± 0.03 V in presence of selected aromatic compounds like benzene, toluene, o-xylene, naphthalene and anthracene. Supportig electrolyte was included by dissolving 0.8 gram atoms of sodium /1 of methanol. The polarization curves of current-potential relationship (Fig.1) showed only one step for the oxidation of acetylacetone. Lesser amount of sodium (0.4 or 0.6 g atoms)/1 of methanol gives extended and drawn out steps(curves b and c).

A linear current-concentration relationship at a potential value of +0.69 V vs SCE was obtained during the anodic oxidation processes (Fig. 1 curve d).

The electrosynthesised products were 3-phenyl 2,4-pentanedione, 3-(p-tolyl)2,4-pentanedione, 3-(o-xylyl)2,4-pentanedione, 3-(β naphthyl) 2,4-pentanedione and 3-(9-anthryl)2,4-pentanedione. However the electrolysis of acetylacetone in the same conditions and in the absence of aromatic compounds gave diacetylacetone (74%) and some polymerized products (9%). These products were analyzed and identified as described in the experimental section. The results obtained are shown in Table 1.

Mechanism of the Anodic Oxidation Processes

The investigation of the current-potential

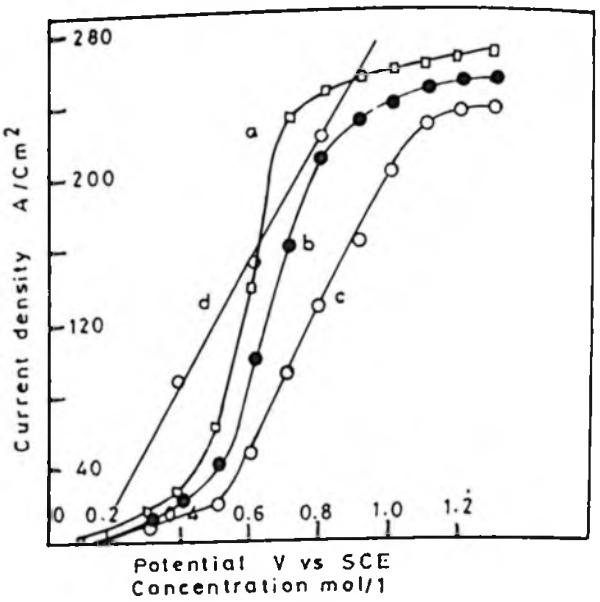


Fig. 1. Anodic oxidation of acetylacetone anions in absolute methanol at 20
a) 0.8 9 atom of Na/l; b) 0.6 g atom of Na/l; c) 0.6 g atom of Na/l
d) Relation between concentration and anodic current at + 0.69 V vs SCE. 20°C.

curves of acetylacetone (Fig. 1a,b,c) and the results of the anodic oxidation of acetylacetone in presence of aromatic compounds (Table 1) indicate that the acetylacetone first loses a proton and the oxidation of acetylacetone anions resulted in the formation of the free radical intermediate species of $CH_3\,\dot{C}OCHCOCH_3$ which dimerises to from a dimer and/or attacks the aromatic compounds forming corresponding 3-aryl 2,4-pentanediones. Also small amounts of polymerization products were formed. This mechanism can be visualized as follows:

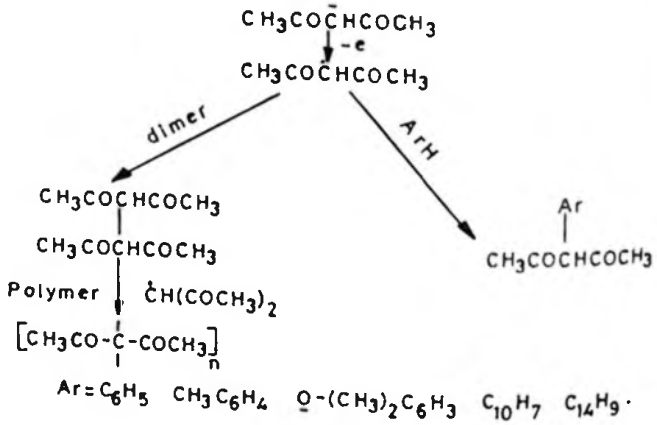


TABLE 1

CONDITIONS AND PRODUCTS: ANODIC OXIDATION OF ACETYLACETONE IN ABSOLUTE METHANOL AT + 1.1 V vs SCE, AT 20°C

Exp	Compounds	Time hr.	Current (A)	Current efficiency (%)	Conversion (a) (%)	Products	Yield (gm. mol)
1	Acetyl acetone	56	0.34 -0.03	13.2	66	$(CH_3CO)_2CHCH(COCH_3)_2$	(3.42, 0.15)
						$[=C(COCH_3)_2]_n$	(1.70, -)
2	Acetyl acetone + C_6H_6	72	0.25 -0.03	12.1	40	$(C_6H_5CH(COCH_3)_2$	(1.59, 0.62)
						$(CH_3CO)_2CHCH(COCH_3)_2$	(1.55, 0.77)
						$[=C(COCH_3)_2]_n$	(0.93, -)
3	Acetyl acetone + $CH_3C_6H_5$	70	0.45 -0.03	6.4	92	$(p\text{-}CH_3C_6H_4CH(COCH_3)_2$	(3.34, 1.74)
						$(CH_3CO)_2CHCH(COCH_3)_2$	(1.37, 0.68)
						$[=C(COCH_3)_2]_n$	(1.04, -)
4	Acetyl acetone + $O(CH_3)_2C_6H_4$	72	0.38 -0.03	8.9	61	$(O\text{-}(CH_3)_2C_6H_3CH(COCH_3)_2$	(4.36, 2.12)
						$(CH_3CO)_2CHCH(COCH_3)_2$	(1.41, 0.70)
						$[=C(COCH_3)_2]_n$	(1.27, -)
5	Acetyl acetone + $C_{10}H_8$	72	0.32 -0.03	10.6	64	$\alpha\text{-}C_{10}H_7CH(COCH_3)_2$	(6.77, 2.97)
						$(CH_3CO)_2CHCH(COCH_3)_2$	(1.19, 0.59)
						$[=C(COCH_3)_2]_n$	(0.64, -)
6	Acetyl acetone + $C_{14}H_8$	72	0.25 - 0.03	10.7	56	$9\text{-}C_{14}H_9CH(COCH_3)_2$	(5.78, 2.08)
						$(CH_3CO)_2CHCH(COCH_3)_2$	(1.38, 0.69)
						$[=C(COCH_3)_2]_n$	(0.868, -)

(a) Conversion = 100 x (total yield of products in mol/amount of starting material in mol).

Thus the formation of arylacetylacetones is by the classical free radical intermediate mechanism of the active methylene compounds [1-10].

It is noteworthy that the yield of acetylacetonylation of aromatic compound is increased with increasing the electron density of the aromatic compounds [9] ($C_{14}H_{10} > C_{10}H_8 > (CH_3)_2C_6H_4 > CH_3C_6H_5 > C_6H_6$) and with increasing the concentration of aromatic compounds. The low yield of the arylacetylacetones may be attributed to the presence of high concentration of acetylacetone free radicals at the anode surface which dimerse and polymerise.

The structures of the anodic oxidation products were confirmed by comparison with those of the authentic samples and found to be identical in all respects (elemental analysis data, m.p., m.m.p., IR, and R_f values in TLC).

This novel method can be used successfully for preparing arylacetylacetone derivatives that can not be obtained by direct methods.

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ELECTROSYNTHESIS OF ORGANIC COMPOUNDS XIII ELECTROCHEMICAL OXIDATION OF BARBITURIC AND 2-THIOBARBITURIC ACIDS*

M.T. Ismail

Department of Chemistry, Faculty of Science, Assiut University, Assiut, Egypt

Electrochemical oxidation of barbituric and 2-thiobarbituric acids was carried out in different nonaqueous solvents (N,N-dimethylformamide, dimethyl sulfoxide and methanol) containing different electrolyte (LiCl, NaOH and $NaOCH_3$) on platinium anode at controlled potential of + 1.4 ± 0.03 V vs SCE at 20°C, for a period of 70-112 hrs. The electrosynthesised compounds were the corresponding dimers, methoxy derivatives and some polymerized products. Suitable mechanisms invoiving the formation of cation and free radical intermediates are suggested.

Also, the anodic oxidation behaviour of the investigated compounds was studied in different solvents containing different electrolytes. The current-potential curves were drawn and one wave for the anodic oxidation processes was observed. The anodic discharge potentials were determined.

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