ELECTROCHEMICAL OXIDATION OF ALLYLBENZENE IN METHANOL

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The electrochemical oxidation (EO) of olefins in nonaqueous solvents has received little attention. The only examples known are the electrochemical alkoxylation and acyloxylation of the double bond in styrenes [1], the allyl oxidation of olefins with internal double bonds [2, 3], and the halofunctionalization of olefins by electrooxidation in the presence of salts of hydrohalic acids [1]. There have also been several reports of the allyl oxidation of olefins of diverse structure by treatment with chemical oxidants, namely compounds of Pb(IV) [4], Hg(II) [4, 5], Cr(VI) [6], Mn(III) [7], and Co(III) [8], by mechanisms involving the formation of intermediate radicals and carbocations.

We here examine the oxidation of allylbenzene (I) in methanol, in order to develop methods of EO and to establish the processes involved.

The electrolysis of solutions of (I) was carried out using a constant current method in an electrochemical cell with undivided cathode and anode spaces, on Pt and carbon anodes. Under these conditions, (I) gave 1-phenyl-1,2,3-trimethoxypropane (II), 3-methoxy-3-phenylprop-1-ene (III), and 3-methoxy-1-phenylprop-1-ene (IV), together with anisaldehyde, benzaldehyde, and (or) their dimethyl acetals.*

One of the main side reactions is the electrochemical hydrogenation of (I) to propylbenzene (V), the contribution of which is highly dependent on the cathode material (Table 1). Hydrogenation of (I) takes place efficiently on an iron cathode (yield of (V) 18%), but does not occur on a lead cathode. In the latter case, however, the total balance of identified reaction products of (I) is <70%, substantial amounts of resinous material being formed. The best results were obtained using a copper cathode, the yield of (V) being no greater than 5%, and the total identified products of the EO of (I) being >90%. All subsequent experiments were carried out using a copper cathode.

Studies of the dependence of the EO of (I) on current density showed that over a wide range of values the product yields were largely independent of current density (Table 2). However, when the current density was reduced from 220 to 50 mA/cm² or less, the current yields of products of the EO of (I) increased by more than 25%. In order to achieve high conversion of (I), subsequent experiments were carried out at a current density of 220 mA/cm².

It follows from the results obtained (Table 3) that the result of the EO of (I) depends on the base electrolyte. When acids are used as the electrolyte, the principal product of the EO of (I) in methanol at a platinum anode is (II). Basic electrolytes guide the EO of (I) towards the preferential formation of (III). When neutral salts are employed, normally in addition to (II) substantial amounts of (III) are formed. Under the conditions used, EO of (I), as shown by separate experiments (see Experimental) did not isomerize, nor did it add methanol.

The results shown in Table 3, together with data for the halfwave oxidation potentials (HOP) of the aromatic ring in arylalkanes (≤ 2.0 V relative to Ag/Ag⁺) [10, 11] and of the double bond in 1-alkenes (≥ 2.7 V relative to Ag/Ag⁺) [12] enable the most likely mechanism of the reaction to be proposed. It appears that oxidation of (I), followed by elimination of a proton from the intermediate cation-radical and further oxidation of the resulting radical, gives the allyl cation (A), methoxylation of which under the reaction conditions affords a mixture of isomeric methoxyphenylpropenes (III) and (IV):

*For a preliminary report, see [9].

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TABLE 1. Influence of Cathode Material on the Electrochemical Oxidation of Allylbenzene (I)* in a Cell with Undivided Cathode and Anode Spaces

	Conversion	Yields of products, percent on (I) reacted							
Cathode	of (I), percent	propylben- zene (V)	1-pheny1-1, 2,3-trimeth- oxypropane (II	3-methoxy- 1-phenyl- prop-1-ene(IV	anisalde- hyde	benzalde- hyde			
Fe Pb Cu	85 64 75	18 5	44 48 65	4 3 3	9 12 11	$\begin{array}{c} 11\\ 6\\ 10 \end{array}$			

*38 mmole of (I), 6 mmole p-TsOH·H₂O in 20 ml of methanol, platinum anode, current density 220 mA/cm², 6.8 F of electricity passed per mole of (I) at 60 \pm 2°C.

TABLE 2. Effect of Current Density on the Electrochemical Oxidation of Allylbenzene (I)*

Current	Conversion of (I), percent	Yield of products, percent of (I) reacted					
density, mA/cm ²		(II)	(IV)	anisalde- hyde	benzalde- hyde	(V)	
220 180 110 50	38 43 52 66 6	$62 \\ 59 \\ 56 \\ 45$	2 2 3 4	9 10 12 11	8 8 9 7	4 3 4 5	

*38 mmole of (II), 6 mmole of p-TsOH·H₂O in 20 ml of methanol, platinum anode, copper cathode, 3.5 F of electricity passed per mole of (I) at 60 \pm 2°C.

TABLE 3. Electrochemical Oxidation of Allylbenzene (I) in Methanol

Expt. no.	Electrolyte	Anode	T., °C	Con- ver- sion of (I) per- cent	Yield of products, percent on (I) reacted ^a					
					' (II)	(III)	(IV)	·(V)	anisal de- hydeb	-benzal de- hydeb
1 2 3 4 5 6 7 8 9 10 11 12 13	$p-TsOH^{C}$ $p-TsOH^{C}$ $H_2SO_4^{d}$ $HCIO_4^{e}$ $Et_4NF\cdot 3HF$ Bu_4HBF_4 $p-TsONa$ $LiNO_3$ $MeOLi$ $MeOLi$ $MeONa$ $p-TsOH$ $MeOLi$	Pt Pt Pt Pt Pt Pt Pt Pt Pt C C	60 30 60 60 60 60 60 60 60 60 60 60	$\begin{array}{c} 62\\ 63\\ 82\\ 94\\ 79\\ 76\\ 63\\ 64\\ 58\\ 32\\ 24\\ 71\\ 45\\ \end{array}$	55 28 44 37 22 43 25 8 4 7 9 23 6	-4 28 36 32 42 59 38 54 42 59 38 54 4 35	$4 \\ 15 \\ 2 \\ 3 \\ 3 \\ 5 \\ 4 \\ 3 \\ 8 \\ 3 \\ 4 \\ 4$	$5 \\ 6 \\ 4 \\ 2 \\ 3 \\ 1 \\ 1 \\ 3 \\ 4 \\ 3 \\ 3 \\ 4 \\ 2$	12 11 12 3 3 1 1 13 1 - - 3 -	$ \begin{array}{c} 10\\ 9\\ 18\\ 19\\ 6\\ 8\\ 11\\ 4\\ 2\\ 3\\ 4\\ 33\\ 4\\ 33\\ 4\\ \end{array} $

^a20 mmole of (I) and 6 mmole of electrolyte in 20 ml of methanol, copper cathode, 6.8 F of electricity passed per mole of (I), current density 220 mA/cm².

^bIn the presence of neutral electrolytes, a mixture of the aldehyde and its acetal was obtained in a ratio of \sim 1:2, and when basic electrolytes were used, the dimethyl acetal was obtained.

^CMonohydrate.

d95% Aqueous solution.

e57% Aqueous solution.

TABLE 4. Halfwave Oxidation Potentials for Allylbenzene (I) and its Electrochemical Oxidation Products in Methanol

Compound	$E_{1/2}$, V
Allylbenzene (I)	1,89
Propylbenzene (V)	1,85
1-Phenyl-1,2,3-trimethoxypropane (II)	1,80
3-Methoxy-3-phenylprop-1-ene (III)	1,95
3-Methoxy-1-phenylprop-1-ene (IV)	1,42
1-(p-Ethoxyphenyl)-1,2,3-trimethoxypropane	1,25
Anisaldehyde	1,63
Anisaldehyde dimethyl acetal	1,64
Benzaldehyde	2,0 [13]

$$\begin{array}{c} \text{OMe} \\ \text{OMe} \\ \text{(III)} \\ \text{PhCH}_2\text{CH} = \text{CH}_2 \xrightarrow{-2e} [\text{PhCH} \cdots \text{CH} \cdots \text{CH}_2]^+ \xrightarrow{\text{MeOH}} \xrightarrow{\text{MeOH}} \stackrel{i}{\longrightarrow} \text{PhCH} = \text{CH}_2 \\ \text{(III)} \\ \xrightarrow{i} \text{PhCH} = \text{CH}_2 \text{OMe} \\ \text{(IV)} \end{array}$$

The methoxyphenylpropenes (III) and (IV) are stable in alkaline and neutral media. Their subsequent fate in the presence of neutral and basic electrolytes is determined by their HOP values (Table 4). The HOP were measured at a rotating platinum electrode using 0.5 M LiClO_4 in acetonitrile, reference electrode Ag/0.1 N Ag⁺ in acetonitrile, scanning rate 20 mV/sec. The HOP for the oxidation of (IV) is much lower than for the original (I) and the methoxyphenylpropene (III) which is isomeric with (IV). Consequently, in the course of the reaction (IV) undergoes rapid further oxidation to (II), whereas (III) is stable up to very high conversion rates of (I):

 $(IV) \xrightarrow{-e} PhCHCHCH2OMe \xrightarrow{MeOH} PhCHCHCH2OMe \xrightarrow{-e} PhCHCHCH2OMe \xrightarrow{-e} PhCHCHCH2OMe \xrightarrow{-e} OMe \xrightarrow{|} PhCHCHCH2OMe \xrightarrow{-e} PhCHCHCH2OMe \xrightarrow{|} OMe \xrightarrow{|} O$

In acid media at 60°C, rapid and complete isomerization (>95%) of (III) to (IV) takes place at a rate which is considerably greater than the rate of EO of (III) (75% after 15 min under the experimental conditions of Exp. 1, Table 3 in the absence of electrical current); the yield of (II) in the EO of (III) or (IV) under the same conditions with the passage of 2.5 F of electricity being 65 and 67% per mole of starting compound respectively.

Hence, when the EO of (I) is carried out in acid media at 60°C, initially the monomethoxylation product of the side chain of the starting material (I) is formed almost exclusively, namely 3-methoxy-1-phenylprop-1-ene (IV):



For the reasons given above, (IV) is oxidized more rapidly than (I). In acid media at 60°C therefore, even at low rates of conversion of (I), the principal product is (II). In addition to methoxylation of the side chain, under the conditions used, methoxylation of the aromatic ring of (I) is possible, to give the allylanisoles (VI):



The presence of an alkoxy-group in the benzene ring of (VI) results in a considerable reduction in its halfwave oxidation potential (by v0.5 V as compared with (I)). Consequently, (VI) rapidly undergoes further EO, so that the main product, at which point the oxidation rate slows down, is anisaldehyde dimethyl acetal (VII):



When the EO of (I) is carried out in the presence of p-TsOH, appreciable amounts of anisaldehyde (up to 15% yield) were found in the reaction mixture. Previously, the EO of the mixture MeOH/CH₂Cl₂/H₂SO₄ has also been shown to involve ring methoxylation, the yield of anisaldehyde being 20% [13].

The EO of (I) in the presence of MeOLi or MeONa is complicated to a considerable extent by the formation of polymeric films on the anode, and probably by the oligomerization of (I)in solution, resulting in the formation of considerable amounts of resinous products. These differences appear to be due to the partial electrooxidation of (I) by an indirect mechanism:

 $\begin{array}{c} \operatorname{MeO}^{-\stackrel{-e}{\longrightarrow}} \operatorname{MeO}^{\bullet} \\ (I) + \operatorname{MeO}^{\bullet} \rightarrow [\operatorname{PhCH} \stackrel{\ldots}{\longrightarrow} \operatorname{CH} \stackrel{\ldots}{\longrightarrow} \operatorname{CH}_{2}]^{\bullet} \\ (B) \stackrel{-e}{\longrightarrow} [\operatorname{PhCH} \stackrel{\ldots}{\longrightarrow} \operatorname{CH}_{2}]^{+} \quad \operatorname{etc.} \\ (A) \end{array}$

Addition of radicals of various types to the double bond in (I) and subsequent reactions result in the formation of oligomers. In our view, confirmation of the indirect mechanism for the oxidation of (I) in the presence of MeOLi is provided by the observed ratio of the oxidation rates of (I) and (V), which have similar HOP values (Table 4). With p-TsOH as base, they should be oxidized at almost identical rates, and this has been confirmed experimentally $(K_{(I)}/K_{(V)} = 1.09 \pm 0.02 \text{ at a platinum electrode in methanol at 60°C})$. It is also known that the removal of α -hydrogen atoms from (I) by tert-butoxyl radicals at 40°C takes place at a rate 2-3 times greater than the rate of the analogous removal from (V) [14]. The latter finding provides an explanation for the observed difference in the rates of electro-oxidation of (I) and (V) with MeOLi as base at 60°C ($K_{(I)}/K_{(V)} = 1.86 \pm 0.05$).

It is noteworthy that when the EO of (I) at a platinum electrode is carried out in either acidic or base electrolytes at temperatures <60°C, the selectivity of the reaction decreases. In the first case, this is due to a decrease in the rate of isomerization of (III) to (IV), and in the second case, apparently, to a decrease in the part played by oligomerization reactions as the temperature is reduced. Using a carbon anode and p-TsOH, the yield of benzaldehyde increased sharply, and in the presence of MeOLi likewise no increase in the selectivity of oxidation of (I) was found.

It is clear from the data shown in Table 3 that the best electrolyte for the EO of (I) to (II) is p-TsOH. When the reaction was carried out in ethanol (under the conditions of Expt. 1, Table 3), 1-pheny1-1,2,3-triethoxypropane was obtained in 25% yield. The reaction failed in propan-2-ol and t-butanol, compounds of types (II)-(IV) being absent, and the (I) being totally converted into resinous products.

EXPERIMENTAL

GC analyses were carried out on an LKhM-8MD chromatograph with a flame ionization detector, in nitrogen, stainless steel columns: 1) 2000 × 3 mm with 15% XF-1150 on Chromosorb W (60-80 mesh); 2) 1000 × 3 mm with 3% OV-17 on Chromatone N-Super (0.125-0.160 mm). PMR spectra were recorded on Tesla BS-497 (100 MHz) and Bruker WM-250 (250 MHz) spectrometers, and mass spectra on a Varian MAT CH-6 and/or a Varian MAT CH-111 (Gnom) spectrometer with a chromatographic inlet (80 eV). Polarizationplots were obtained using a rotating platinum electrode (S = $7.85 \cdot 10^{-3}$ cm²) with a P-5848 potentiostat. All voltammetric measurements were carried out in dry acetonitrile with 0.5 N LiClO₄ as base electrolyte, anolyte volume 25 cm³. The reference electrode was an Ag/0.1 N Ag⁺ electrode in acetonitrile.

Compound	(p, mm Hg)	PMR spectrum, δ,ppm	Mass spectrum, m/z, percent
1-Pheny1-1,2,3-tri- methoxypropane (II)*	128-131 (18)	3,08 s 3,11 s, 3,18 s, and 3,28s (9H, CH ₃ O), super- imposed on signal for (3H, CHOCH ₃ and CH ₂ OCH ₃), 4,21 d and 4,29 d (1H, PhCHOCH ₃), 7,18 m (5H, C ₆ H ₅)	179(2), 178(10), 165(3), 135(4), 133(1), 121(100), 105(17), 91(21), 77(20), 45(18), f. [15]
3-Methoxy-3-phenyl- prop-1-ene (III)	89-91 (20)	3,38 s (3H, CH ₃ O), 4,68 d (1H, CHOCH ₃), 5,26 m (2H, CH ₂ =CH), 6,01 m (1H, CH=CH ₂), 7,20 m (5H, C ₆ H ₅)	$\begin{array}{c} 148(42,M^+),147(24),\\ 133(13),121(100),\\ 117(58),115(66),\\ 105(58),91(69),77(92),\\ 75(47) \end{array}$
3-Methoxy-1-phenyl- prop-1-ene (IV)	125-125(25)	$\begin{array}{c} 3,21 \text{ s} (3\text{H}, \text{CH}_3\text{O}), 4,03\text{d} \\ (2\text{H}, \text{CH}_2), 6,33 (\text{d} 16\text{Hz}, \\ \texttt{t} 6\text{Hz}, 1\text{H}, \text{CH}=), 6,71 \text{d} \\ (16 \text{ Hz}, 1\text{H}), 7,18 \text{ m} \\ (6\text{H}, \text{C}_{6}\text{H}_5) \end{array}$	$\begin{array}{c} 448(63,\ M^+),\ 147(32),\\ 133(14),\ 117(81),\\ 116(63),\ 115(100),\\ 105(38),\ 103(20),\ 91(32),\\ 77(35) \end{array}$
Anisaldehyde	138-142(20)	$3,78 \text{ s} (3\text{H}, \text{CH}_3\text{O}), 6,84 \text{ d}$ and $7,66 \text{ d} (4\text{H}, \text{C}_6\text{H}_4),$ 9,71 s (1H, CHO)	$\begin{array}{c} 136(71,M^+),135(100),\\ 111(12),105(11),92(21),\\ 77(35),63(24),51(15),\\ 50(13) \end{array}$
Anisaldehyde dimethyl acetal	141-143(18)	3,15 s (6H, CH ₃ O), 3,70 s (3H, CH ₃ O), 5,24s (1H, CH), 6,69 d and 7,18 d (4H, C ₀ H ₄)	
1-Phenylprop-2-en- 1-ol	109-111(20)	$\begin{array}{l} 3,32\text{s}\;(1\mathrm{H},\;\mathrm{OH}),4,98\;\text{s}\\(3\mathrm{H},\;\mathrm{CH}_2=\text{and}\mathrm{CHO}),\\ 5,84\text{m}\;(1\mathrm{H},\;\mathrm{CH}),\;7,22\;\text{m}\\(5\mathrm{H},\;\mathrm{C_6H_5}) \end{array}$	
1-Pheny1-1,2,3- triethoxypropane*	143-146(18)	1,21 t, 1,24 t, 1,26 t (9H, CH ₃), 3,52 m (9H, CH ₂ O and CHO), 4,34d and 4,39 d (1H, PhCHO), 7,34 m (5H, C ₆ H ₃)	$\begin{array}{c} 207(3),206(7),193(3),\\ 179(9),149(17),\\ 135(100),107(40),\\ 105(24),91(28),79(29),\\ 77(24) \end{array}$
p-Ethoxyallyl- benzene	99-102(18)	1,26 t (3H, CH ₃), 3,20 d (2H, PhCH ₂), 3,83 q (2H, CH ₂ O), 4,87 m (2H, CH ₂ =), 5,76 m (1H, CH), 6,89 d and 7,28 d (4H, C_6H_4)	
1-(p-Ethoxyphenyl)- 1,2,3-trimethoxy- propane*	170–173(25)	1,41 t and 1,42t $(3H, CH_3)$, 3,20 s, 3,22 s, 3,25 s, 3,26 s, 3,34 s, and 3,46 s $(9H, CH_3O, superimposedon signal for 3H,CHO and CH2O), 4,01 q(2H, CH_3CH_2O), 4,19 d4,28 d (1H, ArCHO),6,88 d and 7,23 d (4H,CeH.)$	$\begin{array}{c} 222 (2), \ 209 (1), \ 191 (2), \\ 178 (4), \ 166 (11), \\ 165 (100), \ 137 (53), \\ 133 (3), \ 121 (18), \ 107 (15), \\ 45 (22) \end{array}$

TABLE 5. Physicochemical and Spectral Properties of the Reaction Products

*Composition confirmed by elemental analysis.

The cinnamyl alcohol grade was laboratory reagent grade (East Germany), used without further purification. The p-ethoxybromobenzene and allyl bromide were of pure grade, further purified by distillation. Allylbenzene was of reagent grade, purified by distillation over sodium. $LiNO_3$, $LiClO_4$, NH_4ClO_4 , H_2SO_4 , and $HClO_4$ were of chemically pure grade, and were used without further purification. Toluene-p-sulfonic acid was pure grade, recrystallized from chloroform.

<u>Electrochemical Oxidation of Allylbenzene (I) in Methanol (General Method)</u>. In a nondiaphragm cell with external cooling (distance between electrodes 5 mm) fitted with a magnetic stirrer, thermometer, and reflux condenser were placed 38 or 20 mmole of (I), 6 mmole of electrolyte, and 20 ml of dry methanol, and electrolysis was carried out with constant current flow. The reaction mixture was analyzed by GC, evaporated to a volume of 5 ml, 75 ml of water added, and washed with water. The ether extract was dried over Na₂SO₄, evaporated, and the residue distilled in vacuo to separate the oxidation products. The conversion of (I) and yields of oxidation products (accordng to GC) are given in Tables 1-3, and the spectral and physicochemical properties of the products of the oxidation of (I) in Table 5.

<u>Isomerization and Acid-Catalyzed Addition of Methanol to (I)</u>. No isomerization or methoxylation of the double bond in (I) occurred when (I) was boiled in methanol in the presence of toluene-p-sulfonic acid, sulfuric acid, or MeOLi as in experiments 1, 3, and 11 (Table 3) without passage of current.

1-Phenylprop-2-en-1-ol was obtained by reacting PhMgBr with acrolein, yield 70%.

<u>3-Methoxy-3-phenylprop-1-ene (III)</u> was obtained by methylating 1-phenylprop-2-en-1-ol with methyl iodide in DMF in the presence of BaO, yield 85%.

Isomerization of 3-Methoxy-3-phenylprop-1-ene (III). When (III) was boiled in methanol in the presence of toluene-p-sulfonic acid as in experiment 1, Table 3, without passage of current through the solution, after 15 min the (III) was isomerized to the extent of 75%, and after 30 min 98% to 3-methoxy-1-phenylprop-1-ene (IV). When (III) was boiled in methanol in the presence of $LiNO_3$ or MeOLi as in experiments 8 and 11, Table 3, after 3.5 h no isomerization of (III) to (IV) was observed.

<u>3-Methoxy-1-phenylprop-1-ene (IV)</u> was obtained by methylating cinnamyl alcohol, yield 95%, and was also isolated by fractional distillation of the reaction mixture from experiment 11, Table 3.

<u>Anisaldehyde dimethyl acetal</u> was obtained by the electrochemical oxidation of p-methoxytoluene [16].

<u>1-Phenyl-1,2,3-trimethoxypropane (II)</u> was obtained by the electrochemical oxidation of 38 mmole of (I) at a platinum anode in the presence of 6 mmole of toluene-p-sulfonic acid in 20 ml of methanol, using 6 F of electricity per mole of (I) taken, current density 220 mA/cm², conversion of (I) 80%. Vacuum distillation gave 4 g of (II), yield 45% on (I) taken.

<u>1-Phenyl-1,2,3-triethoxypropane</u> was obtained similarly, by passing 7.8 F of electricity per mole of (I) in ethanol, yield 25%.

<u>1-(p-Ethoxyphenyl)-1,2,3-trimethoxypropane</u>. Reaction of p-ethoxyphenyl-magnesium bromide with allyl bromide gave p-ethoxyallylbenzene, yield 75%. Electrochemical oxidation of p-ethoxyallylbenzene using 4.5 F of electricity per mole of starting material gave 1-(p-ethoxy-phenyl)-1,2,3-trimethoxypropane, yield 48%.

CONCLUSIONS

1. Electrochemical oxidation of allylbenzene in methanol in the presence of basic electrolytes affords 3-methoxy-3-phenylprop-1-ene (III), but when acidic electrolytes are used, 1-phenyl-1,2,3-trimethoxypropane is formed preferentially. The greatest selectivity of methoxylation both with basic and acidic electrolytes is attained at a platinum anode at 60°C.

2. The (III) which is formed in the first stage of the oxidation of allylbenzene in the presence of toluene-p-sulfonic acid undergoes quantitative isomerization to 3-methoxy-1-phenylprop-1-ene.

3. Allylbenzene is efficiently hydrogenated at an iron electrode in methanol at 60°C, but at a lead cathode under similar conditions hydrogenation is completely suppressed.

LITERATURE CITED

1. S. Torii and T. Siroi, J. Synth. Org. Chem. Japan, <u>37</u>, 915 (1979).

2. T. Shono and A. Ikeda, J. Am. Chem. Soc., <u>94</u>, 7892 (1982).

- 3. T. Shono, A. Ikeda, J. Hayashi, and S. Hakozaki, J. Am. Chem. Soc., <u>97</u>, 4261 (1975).
- 4. K. B. Wiberg and S. D. Nielsen, J. Org. Chem., <u>29</u>, 3353 (1964).

5. Z. Rappoport, S. Winstein, and W. G. Young, J. Am. Chem. Soc., <u>94</u>, 2320 (1972).

6. W. G. Dauben, M. Lorber, and D. S. Fullerton, J. Org. Chem., <u>34</u>, 3587 (1969).

7. J. R. Gilmore and J. M. Mellor, J. Chem. Soc., C, 2355 (1971).

8. M. Hirano, K. Nakamura, and T. Morimoto, J. Chem. Soc., Perkin Trans., 2, 817 (1981).

- 9. G. I. Nikishin, M. N. Elinson, and I. V. Makhova, Izv. Akad. Nauk SSSR, Ser. Khim., 1919 (1984).
- 10. H. Lund, Acta, Chem. Scand., <u>11</u>, 1323 (1957).
- 11. W. C. Neikam, G. R. Dimeler, and M. M. Desmond, J. Electrochem. Soc., <u>111</u>, 1190 (1964).
- 12. M. Fleischman and D. Pletcher, Tetrahedron Lett., 6255 (1968).
- 13. M. Rakoutz, D. Michelet, B. Brossard, and J. Varagnat, Tetrahedron Lett., 3723 (1978).
- 14. C. Walling and W. Thaler, J. Am. Chem. Soc., <u>83</u>, 3877 (1961).
- 15. H.-F. Gruzmacher and J. Winkler, Org. Mass Spectrom., 295 (1968).
- 16. A. Nilsson, U. Palmquist, T. Pettersen, and A. Ronlan, J. Chem. Soc., Perkin Trans. 1, 708 (1978).

ELECTROCHEMICAL HYDRODIMERIZATION OF CARBONYL COMPOUNDS IN APROTIC MEDIA

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In the investigation of the process of the electroreduction (ER) of aromatic carbonyl compounds in aprotic media, it was established that the primary products at the first stage of the electrode reaction are anion-radicals (ARs); the products of the second stage are dianions [1, 2]. The assumption is thereby made that the main reaction of the ARs in the aprotic media is dimerization, which leads to pinacone (PC). Under these conditions, the dianion, which possesses significantly higher basicity, can be protonated with the formation of the corresponding alcohol.

We previously proposed [3, 4] a method of calculating the rate constants for the reactions of the ARs and dianions under conditions where the specific interactions of these entities with the components of the solution (e.g., in the solutions of tetraalkylammonium salts in dry DMF) can be ignored. In the framework of such an approach to the ER of aromatic carbonyl compounds, neither PC nor alcohol can be the main products of the electrolysis due to the competing rections of the "head-tail" type under the indicated conditions. This conclusion is consistent with the results of the preparative ER of carbonyl derivatives of the thiophene series [5, 6].

However, the practically quantitative yield of PC is ascertained as the result of the electrolysis of acetophenone (I) in dry MeCN and DMF in the presence of quaternary ammonium salts in [7, 8]. Moreover, the solutions of the tetraethylammonium salts in the dry aprotic solvents are recommended in [8] as the optimal media for the preparative isolation of the aliphatic-aromatic PCs. This conclusion is in contradiction with the data of [9], where it was shown that the cyanidation products are formed together with the PCs by the electrolysis of aromatic ketones in MeCN. The given work is devoted to a more detailed investigation of the process of the ER of (I) in "dry" DMF at a controlled potential.

EXPERIMENTAL

<u>Reagents</u>. The DMF was first dried over molecular sieves; it was then distilled in vacuo. The water content according to Fischer was <0.04%. In a series of cases, the DMF was passed through a layer of calcined neutral Al_2O_3 instead of the distillation. The salts of the electrolyte present were dried in vacuo at 60°C before utilization. The commercial acetophenone (I) was purified by fractional distillation in vacuo.

<u>Electrolysis</u>. The electrolysis was performed at a controlled potential with the aid of a P-5848 potentiostat (Gomel') in cells with a glass diaphragm. The cathode was mercury; the anode was platinum gauze. The potentials were measured relatively to the adjustable

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