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THE ELECTROCHEMICAL METHOXYLATION OF METHOXYBENZENES AND RELATED COMPOUNDS

THE MECHANISM OF ELECTROCHEMICAL METHOXYLATION OF 1,4-DIMETHOXYBENZENE

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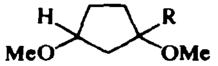
Abstract—Anodic oxidation of benzenoid aromatic ethers in methanolic KOH soln at a platinum electrode constitutes a one step method for the synthesis of the rare class of compounds, herein designated as the quinone diketals. The mechanism of conversion of 1,4-dimethoxybenzene to the diketal of *p*-benzoquinone, based on the evidence accumulated, is considered to proceed *via* discharge of the adsorbed aromatic compound, followed by nucleophilic reaction of the solvent system with the electrogenerated cationic species. The quinone diketal products resulting from anisole, 1,4-, 1,2-, and 1,3-dimethoxybenzene, 9,10-dimethoxyanthracene and benzodioxane have been established. In contrast methyl benzoate, anisonitrile, and benzene were found to be unreactive in agreement with a direct discharge scheme which does not involve methoxy radicals.

INTRODUCTION

The past decade has witnessed a series of significant advances in the field of electro-organic chemistry which has brought renewed interest to bear on this relatively old branch of chemistry. A number of reviews have recently appeared[1-5] presenting the considerable progress achieved in understanding the roles of the electrochemical reaction variables (electrode potential, current density, electrode material, adsorption of substrate and/or solvent, etc) as they relate to electro-organic processes. As a result of these advances, the organic chemist now has at his disposal a valuable method for conveniently synthesizing products unique in their structure and/or mode of formation. This report details the electrochemical methoxylation of aromatic compounds which was partially communicated earlier,[6] as well as evidence for the mechanism of reaction.

In the early 1950's Clauson-Kass and coworkers discovered that electrochemical oxidation of furans at platinum anodes in MeOH containing NH_4Br as the supporting electrolyte constituted an excellent method for the synthesis of 2,5-dimethoxy-2,5-dihydrofurans (**1**).[7] The reaction was conceived as a logical alternative to the already known chemical method of preparation of **1** in which furans are treated with methanolic bromine solution.[8,9] The advantage of the electrochemical method consists in that only catalytic amounts of NH_4Br can substitute for stoichiometric quantities of bromine. It was subsequently found[7] that non-halogen containing supporting electrolytes such as H_2SO_4, $NaOCH_3$ and $NaNO_3$ could also be used. Moreover, while conversion of furans carrying electronegative substituents could not be achieved chemically, the electrochemical method could be applied successfully using $MeOH/H_2SO_4$ solutions. It thus became clear that electrochemical ethoxylation proceeds by an alternative mechanism not requiring electrogenerated halogen.‡

Since the Clauson-Kaas reaction destroys the aromatic character of furans, the question arose as to whether benzenoid aromatics could be induced to behave similarly.



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RESULTS AND DISCUSSION

1. *Products*

A variety of benzenoid aromatics was electrolyzed in a one compartment cell using Pt as the anode and Ni as the cathode materials. Reactions were carried out in 1% KOH/MeOH solution using an anode current density of about 0·025 Acm^{-2}.

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‡The electrochemical reaction might involve reaction of the furan with electrochemically generated OMe radicals or preferably reaction of a cationic species (cation radical or dication derived from the discharge of the furan moiety followed by reaction with solvent. (See reference 1, p. 461 for arguments in favor of the latter scheme).

Table 1. Electrochemical methoxylation of aromatic compounds

Starting material	N$_{\frac{1}{2}}$^{1}(V vs SCE)	Nlectrolysis product(s) (% yield)[b]
Methyl benzoate	> 3[c]	nil[d]
Anisonitrile	> 3[c]	nil[d]
Benzene	2·3[11]	nil[d]
Anisole	1·76[12]	mixture of *o*,*m*, and *p*-dimethoxybenzenes in ratio 39: < 3: 58 (low); quinone diketals
1,4-Dimethoxybenzene	1·34[12]	3,3,6,6-tetramethoxy-1,4-cyclohexadiene (88)
1,3-Dimethoxybenzene	—	1,2,4-trimethoxybenzene (< 5); 2,3,3,6,6-pentamethoxy-1,4-cyclohexadiene (67) unidentified polymethoxylated product
1,2-Dimethoxybenzene	1·12[12]	1,2,4-trimethoxybenzene (15) 5,5,6,6-tetramethoxy-1,3-cyclohexadiene (16) 2,3,3,6,6-pentamethoxy-1,4-cyclohexadiene (9); hexamethyl *cis*, *cis*-orthomuconate (5·3)
9,10-Dimethoxyanthrancene	0·98[12]	9,9,10,10-etramethoxy-9,10-dihydroanthracene (32)
Benzodioxane	—	*trans*-4a,8a-dimethoxy-4a,8a-dihydro-1,4-benzodioxane (31); unidentified products.

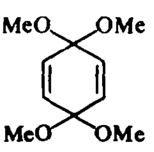
[a]Determined in MeCN/ClO_4^- at Pt; [b]P_2t anode; MeOH/KOH Solution; [c]Estimated; [d]Starting material recovered

External cooling was applied in all cases. The results of these studies are summarized in Table 1.

The methoxybenzene class of aromatics afforded a relatively rare class of compounds which are herein designated as quinone diketals. Thus 1,4-dimethoxybenzene (1,4-DMB) gave the *p*-benzoquinone diketal **2** with a 65% current efficiency (CE). The yield of this previously unknown diketal could be easily raised to 88% by extending the reaction time. The CE losses in all these reactions are accounted for by the oxidation of the solvent to formaldehyde, formic acid, and carbon monoxide.[10] The structure of **2** was established by NMR spectroscopy and by quantitative hydrolysis in dilute aqueous hydrochloric acid to *p*-benzoquinone.

Subsequent potentiostatic studies have shown that the maximum current efficiency for the production of **2** lies at anode potentials greater than 1·4 V vs SCE. Separation of the electrolysis vessel into anode and cathode compartments had no effect on the CE for the formation of **2**, implying that 1,4-DMB and **2** are protected from cathodic attack by preferential discharge of solvent. Therefore for all practical purposes quinone diketals may be conveniently prepared in non-compartmentized cells. In addition, controlled potential methods[13] are not required provided that the optimum electrode potential or corresponding current density is maintained. These electrochemical parameters were evaluated only for the case of 1,4-DMB. The yields and current efficiencies for most of the reactions listed in Table 1 could be substantially improved through potentiostatic studies.

It is of interest that **2** could be formed in comparable current efficiency at amorphous carbon (50·3%) and at vitreous carbon (54·6%) anodes. Therefore, these processes do not depend on a specific surface or catalytic property of Pt.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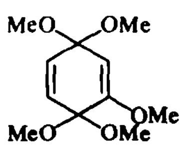
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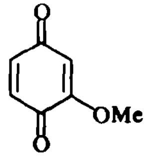
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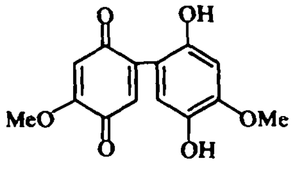
Electrochemical methoxylation of 1,3-dimethoxybenzene proceeded smoothly to give 2,3,3,6,6-pentamethoxy-1,4-cyclohexadiene (**3**) in 67% yield along with a small amount of 1,2,4-trimethoxybenzene and a polymethoxylated compound tentatively identified as 3,3,4,4,5,5,6,6-octamethoxycyclohexene. Hydrolysis of **3** in dilute acid gave a high yield of the intensely blue biphenyl quinhydrone (**5**) by way of methoxy-*p*-benzoquinone (**4**) which has been previously shown[14,15] to couple to give **5** under acid conditions. The structure of **3** and the intermediacy of 1,2,4-trimethoxybenzene were confirmed by electrolysis of the latter under similar conditions to give **3** in 89% yield.

When 1,2-dimethoxybenzene was subjected to the electrolysis conditions, a mixture of four products resulted. Fractional distillation afforded the already known diketal **3** (9%), 1,2,4-trimethoxybenzene (15%), the *o*-benzoquinone diketal **6** (16%), and 5·3% of a ring cleaved product which was shown to be hexamethyl *cis*,*cis*-orthomuconate (**7**). The diketal **6** could be reductively hydrolyzed with Zn/dilute HCl to give catechol in 25% yield (and polymers of *o*-benzoquinone), whereas hydrolysis of the diortho ester **7** gave dimethyl *cis*,*cis*-muconate (**8**) quantitatively. Spectroscopic data (NMR, UV, IR) were clearly consistent with the proposed structures. That the diketal **6** was the



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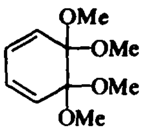

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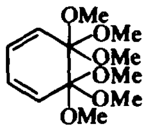

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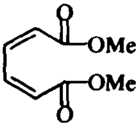

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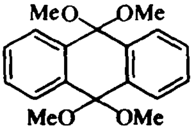

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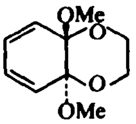

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precursor of 7 was confirmed by submitting 6 to further electrolysis whereupon the ortho ester 7 was obtained in 77% yield.

In a similar manner, 9,10-dimethoxyanthracene was converted to the corresponding diketal 9. Benzodioxane gave among other products, a readily isolatable, crystalline substance identified as *trans*-4a,8a-dimethoxy-4a,8a-dihydro-1,4-benzodioxane[16] (10). Significantly, however, methyl benzoate, anisonitrile, and benzene could not be methoxylated. Anisole, gave methoxylation products including dimethoxybenzenes and quinone diketals in very low overall current efficiency.

2. *Mechanism of electrochemical methoxylation*

Two schemes which could account for electrochemical methoxylation of 1,4-DMB are depicted in Fig 1. The quinone diketal 2 could be formed *via* reaction with electrochemically generated methoxy radicals (Eq. 1, 2). Alternatively, the aromatic ring could discharge directly at the anode to give a cationic species (cation radical, path 3 (a); dication, path 3 (b)) which upon reaction with the solvent (and for Eq. 3 (a), a further electron transfer) would lead to the product 2. Each of these schemes theoretically requires 2 f/mole.

Current-potential curves for oxidation of 1,4-

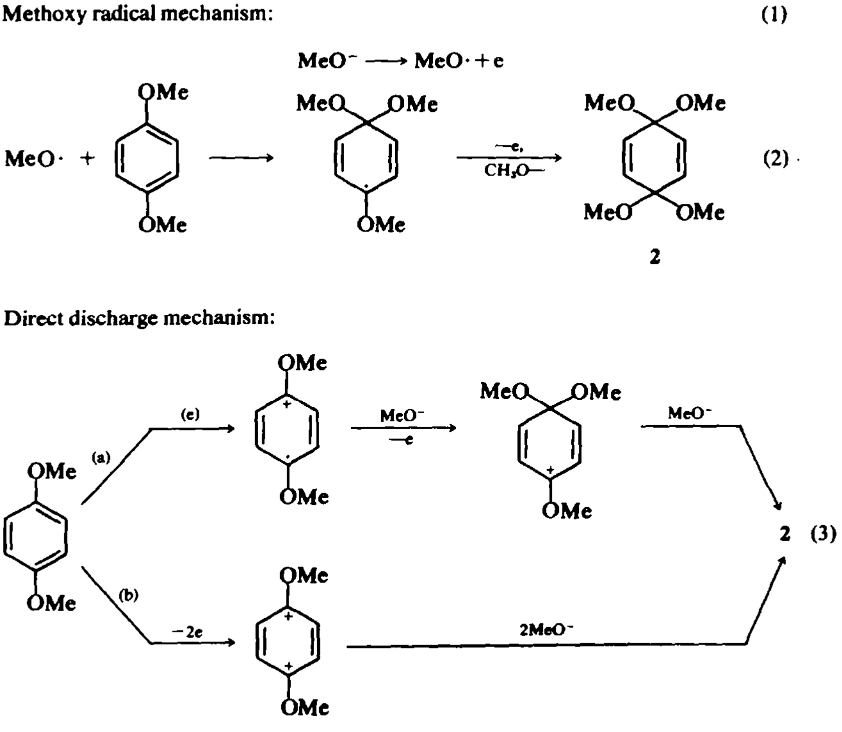

Fig 1. Mechanisms of electrochemical methoxylation of 1,4-dimethoxybenzene

DMB in 0·5 M KOH/MeOH were inconclusive because of the low anodic solvent discharge potential (about 0·7 V). However, it was eventually found that the useful solvent "window" may be extended from 0·7 to 1·0 V by pre-electrolysis for a short period of time, by "aging" the solution in a polyethylene container for three months, or by introducing a small amount of carbon dioxide gas.* Several other substances, including cyanide and cyanate are known[17] to increase the useful anodic range of methanol up to about 1·7 V. Evidence has been accumulated which suggests that these materials are adsorbed on the anode blocking sites normally available for solvent discharge.

Conclusive evidence that 1,4-DMB is converted to **2** *vis* a direct discharge scheme (3) and not by OMe radicals† is shown by current-potential data obtained in 0·5 M KOH/MeOH containing a little carbon dioxide: the aromatic ether discharges more easily than the solvent (Fig 2). Moreover a Tafel plot[18] of 1,4-DMB oxidation corrected for background (solvent oxidation) had a slope of 116 mV/decade suggesting that the rate determining step may involve discharge of the aromatic compound to the corresponding cation radical. An electrolysis conducted at 1·6 V in this lightly carbonated solution gave **2** in 64·9% CE. Hence, carbon dioxide (or rather carbonate as it exists in solution) only serves to inhibit methanol oxidation and does not affect product formation.

The unusual but facile conversion of the diketal **6** to the *bis*-ortho ester **7** is thought to occur because of the presence of four vicinal oxygen atoms in **6**, an arrangement which ought to be energetically unfavorable. Spectroscopic evidence in support of this proposal has already been cited.[6] Ring opening could then be envisioned to proceed *via* direct discharge at the anode to give an adsorbed cationic species, which through nucleophilic attack by solvent would proceed to the observed product **7**.

The conversion of 1,3-dimethoxybenzene to a mixture of **3** and its precursor 1,2,4-trimethoxybenzene is interesting mechanistically. Fig 3 depicts several routes to 1,2,4-trimethoxybenzene involving either loss of the elements of MeOH from the cyclohexadiene **11** or loss of a proton from the carbonium ion **12**. To differentiate between the two routes, an electrolysis was conducted with 1,3-dimethoxybenzene labelled with $-OC^{14}H_3$. Product **3** possessed the same specific activity as

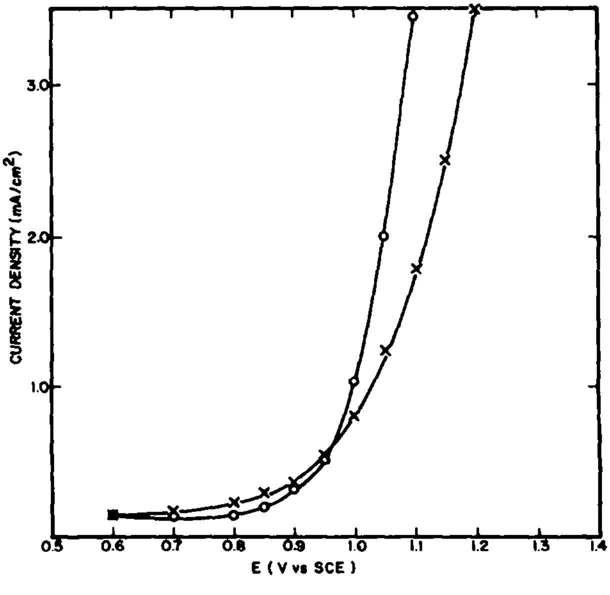

Fig 2. Current-potential curves at Pt (10 cm^2) at 15°C. ×, 0·5 M KOH/MeOH/CO_2; ○, 0·1 M 1,4 Dimethoxybenzene in 0·5 M KOH/MeOH/CO_2.

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*Electrochemical oxidation of 1,4-DMB in each of these "treated" solutions gave **2**; however, **2** was formed in 82·5% CE in the "aged" system compared with 65% CE in the other two solutions. It seems possible that a polymer additive (now under investigation) leached out of the polyethylene container, may be responsible for the enhanced yield. Pre-electrolysis could give CO, CO_2, HCHO, and HCO_2H according to the literature,[10] all of which are known to adsorb on Pt anodes.

†Photolysis of N-methoxyphenanthridium perchlorate in CH_3CN solution generates methoxy radicals. In this solution anisole is reported[19] to give a 21·6% yield of methoxylated products in *o*:*m*:*p* = 79:trace:21 (*cf* Table 1). Benzene and benzonitrile which are inert under the electrochemical conditions because of their relatively high anodic oxidation potentials, have been methoxylated in the above photochemical procedure. Evidence that methoxy radicals are not involved in these electrochemical reactions is thus provided.

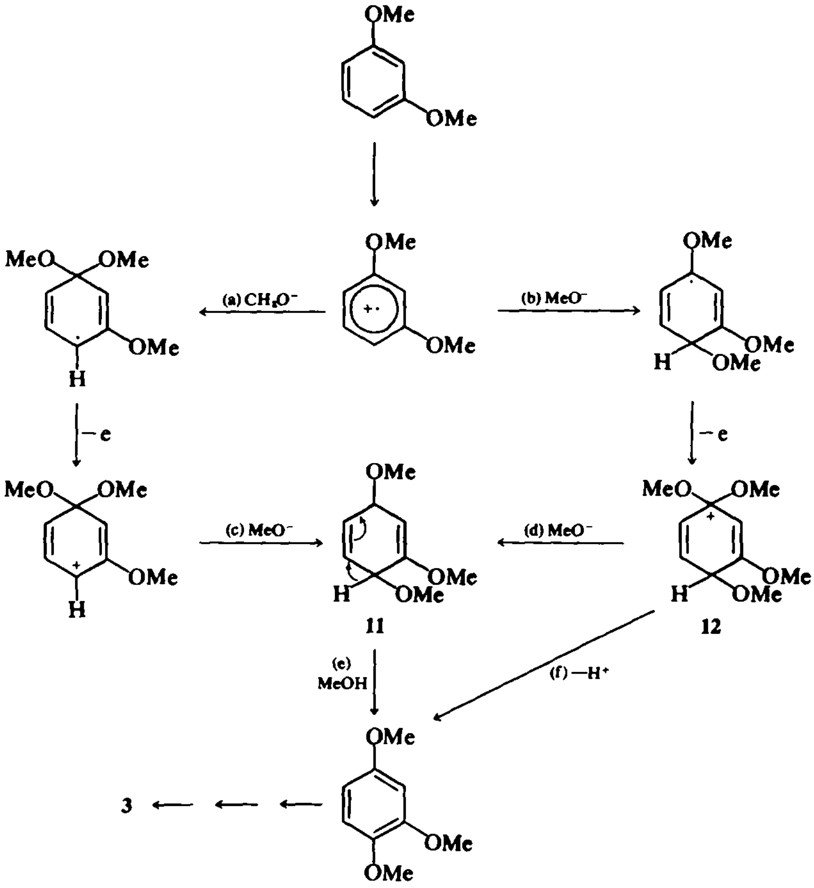

Fig 3. Electrochemical oxidation of 1,3-dimethoxybenzene

the starting material, thus establishing that no OMe groups are lost from the ring during electrolysis. This evidence supports route (b → f) as a logical reaction pathway.

EXPERIMENTAL

Constant current electrolyses were conducted as described earlier.[6] Mechanistic studies and controlled potential electrolyses were carried out using a Par$^{\mathrm{TM}}$ Model 173 Potentiostat with a 3-compartment H-cell at 15°. The electrodes were Pt (10 cm^2) and the reference was a saturated calomel (SCE). Electrolyses were also conducted with amorphous carbon (Union Carbide YBD) and vitreous carbon (Atomergic) anodes. An Acromag digital integrator served as a coulometer. Reagent grade CH_3OH and KOH were employed throughout without further purification.

Molecular weight (MW) measurements (Rast) were determined with *d*-camphor, mp 178° (Eastman Reagent Grade).

UV spectra were determined with a Beckman DK-2 spectrophotometer, IR spectra with a Perkin-Elmer Infracord, and NMR spectra with a Varian Model V-4302 operating at 60 Mc sec^{-1}. Vapour phase chromatography was carried out with a Perkin-Elmer Vapour Fractometer, Apiezon on glass beads.

1. *Electrolysis of* 1,4-*dimethoxybenzene*

(a) *At constant current, small scale at* Pt. To a magnetically stirred soln of 2 g KOH in 250 ml of MeOH at 0° was added 13·8 g (0·100 mole) of 1,4-DMB. This was electrolyzed at 2·0 A (cell voltage 3·6–3·8 V) for 3 hr in an uncompartmentized cell at a Pt gauze anode (cd about 0·025 Acm^{-2}) and a Ni cathode. The cell was provided with a cold finger for internal cooling at the anode. After electrolysis the solution was concentrated on a rotary evaporator at 30–40°/20–30 mm Hg. To the residue was added 250 ml of water and this was extracted with 3, 50 ml portions of ether. The organic extract was dried over anhydrous magnesium sulfate, filtered, and concentrated leaving 16 g of an oily solid. Crystallization from light petroleum (40–60) afforded 15 g (0·075 mole; 75% yield, 66% CE) of 2, m.p. 40–41°. Sublimation of this solid at 35°/0·1 mm Hg raised the m.p. to 42·0–42·5°. Calc. for $C_{10}H_{16}O_4$: C, 59·98; H, 8·05%; MW, 200). (Found: C, 60·18; H, 7·89; MW, 217. Calc. for $C_{10}H_{16}O_4$: C, 59·98 H, 8·05%; MW, 200). The IR spectrum (Nujol^{R} mull) had characteristic peaks at 1645 (w), 1110 (s), 1070 (s), 1020 (s), 975 (s), 960 (s) cm^{-1}. The NMR spectrum in CCl_4 exhibited only two peaks at 6·75τ (ketal OMe) and 4·03τ (olefinic H) with a ratio of areas of 3 : 1 respectively.

Hydrolysis of 2 was carried out by dissolving 1·00 g (0·00500 mole) in 15 ml of water, followed by addition of 5 ml of 10% HCl aq. After 5 min, the yellow solid (needles) was filtered and sublimed at 60°/0·01 mm Hg to give 0·535 g (0·00495 mole; 99% yield) of *p*-benzoquinone, m.p. 113–114°. A mixed m.p. with authentic *p*-benzoquinone was not depressed and the IR spectra (Nujol^{R}) were identical. The reaction of 2 with BF_3 etherate in benzene was previously described.[6]

(b) *At constant current, larger scale at* Pt. A larger scale electrolysis was carried out with 200 ml of MeOH containing 2 g KOH. The aromatic was added in 5 to 10 g portions over a period of 2 hr to a total of 69·0 g (0·500 mole) of 1,4-DMB, while a current of 5A (cd 0·06 Acm^{-2}, cell voltage 7–8V) was passed for a total of 24 hr. The temperature of the electrolsate ranged from 25 to 40°. The residue, after work-up, gave 88 g (0·44 mole; 88% yield) of 2, m.p. 39–41°.

(c) *Controlled potential electrolyses at* Pt. Controlled potential electrolyses were conduted in a 3-compartment H-cell at 15° using Pt electrodes (10 cm^2) and a SCE reference. The anolyte consisted of 100 ml of 0·50 M KOH/MeOH containing 0·10 M 1,4-DMB. The catholyte was 0·50 M KOH/MeOH. After passage of 1000 to 2000 C the anolyte was concentrated *in vacuo*, taken up in water and diethyl ether, and the organic layer extracted. This was dried over $MgSO_4$, filtered, and concentrated to give about 1·3–1·5 g of oily residue. Analysis of NMR spectroscopy in $CDCl_3$ showed only the presence of 1,4-DMB and 2. The CE (calculated on the basis of 2 f/mole required theoretically was determined at the following potentials: 1·00, 1·10, 1·45 and 1·60 V vs SCE. The respective CE's were 19, 51, 65 and 65%.

(d) *Controlled potential electrolysis at carbon anodes*. Electrolysis of 2·76 g (0·0200) 1,4-DMB was carried out at 15° in 100 ml of 0·5 M KOH/MeOH. A one-compartment cell was used with an Atomergic vitreous carbon anode (2·5 cm × 3 mm diam), a Pt (10 cm^2) cathode, and an isolated SCE reference electrode. The electrolysis was conducted at 1·50 V vs SCE. After passage of 5500 C the electrolysate was worked up to give 3·4 g of crude product which on NMR analysis showed the presence of 22·2% 1,4-DMB and 77·8% of the diketal 2 (54·6% CE). In a similar manner electrolysis at a Union Carbide YBD amorphous carbon anode at 1·30 V gave 2 in 50·3% CE.

2. *Electrolysis of* 1,2- *and* 1,4-*dimethoxybenzene*

These reactions were carried out as in 1(a). The products were described earlier.[6]

3. *Preparation of methyl-*C^{14}-1,3-*dimethoxybenzene*

A solution of 130 ml of dithyl ether containing 21·5 g (0·10 mole) of N-methyl-N-nitroso-*p*-toluenesulfonamide (Aldrich, "Diazald") and 0·0055 g (0·000030 mole) of N-C^{14}-methyl-N-nitroso-*p*-toluenesulfonamide (New England Nuclear Corp., "Diazal-C^{14}") having a specific radioactivity of 0·10 millicuries, was added dropwise to a solution of 5 g of KOH in 25 ml of 95% alcohol plus 8 ml of water in a 100 ml distilling flask, fitted with a condenser for downward distillation. The condenser was connected to two 250 ml flasks in series cooled in an ice-bath. The second flask contained a solution of 3·3 g (0·030 mole) of resorcinol in 31 ml of ether. After the ethereal diazomethane soln had been transferred from the first receiver to the reaction flask by warming at 50°, the latter was disconnected, closed, except for a fine capillary opening, and allowed to sit at room temp in the dark for one week. A drop of BF_3-etherate was then added (to destroy excess diazomethane) along with 11 g of 1,3-dimethoxybenzene. The solvent was removed *in vacuo* and the residue distilled to give 13·5 of liquid, b.p. 94–101°/13 mm. This was allowed to stand over 3 g KOH for 6 hr, filtered, and redistilled to give 12·7 g (0·092 mole) of C^{14}-labelled 1,3-dimethoxybenzene, giving 5·59 × 10^8 counts min^{-1} $mole^{-1}$ (Nuclear Chicago Liquid Scintillation Counter).

4. *Electrolysis of methyl-*C^{14}-1,3-*dimethoxybenzene*

Methyl-C^{14}-1,3-dimethoxybenzene (10·5 g, 0·076 mole) was electrolyzed as before at 25° at a current of 4·0 A for 5·5 hr. Distillation of the crude product gave 13·1 g (0·057 mole; 75% yield) of 3, b.p. 92–94°/0·2 mm, n_D^{27} 1·4775. A redistilled sample, b.p. 103°/0·4 mm, n_D^{27} 1·4765, measured for radioactivity under the same conditions as for starting material, showed 5·54 × 10^8 counts min^{-1} $mole^{-1}$.

5. *Electrolysis of* 5,5,6,6-*tetramethoxy*-1,3-*cyclohexadiene* (6) *at* Pt

The diketal 6 (5·2 g, 0·026 mole) was electrolyzed as before at 20° for 6 hr at 4·0 A. The crude, gummy solid obtained after concentration of the electrolysate was crystallized from 95% EtOH, giving 5·3 g (0·020 mole; 77% yield) of hexamethyl *cis,cis*-orthomuconate, m.p. 96–98°. The NMR and UV spectra of this material and that isolated previously (Experimental, Part 2.) were identical.

6. *Electrolysis of* 9,10-*dimethoxyanthracene at* Pt

9,10-Dimethoxyanthracene was prepared according to the method of Meyer[20] from anthraquinone. Electrolysis was carried out with 11·9 g (0·050 mole) of the aromatic in 250 ml MeOH containing 2 g KOH at 20° at 4·0 A for 3·75 hr. The aromatic was almost insoluble in the system and at no time during the reaction was solution complete. Work-up was accomplished by pouring the electrolysate into 250 ml of water. The solid was filtered off and dried in air (crude weight 12·0 g, m.p. 130–145°). This was twice recrystallized* from benzene to give 4·8 g (0·016 mole, 32% yield) of the anthraquinone diketal 9, m.p. 159·5–161·0°, colorless cubic crystals. (Found: C, 72·19; H, 6·80; OMe, 39·3. Calc. for $C_{18}H_{20}O_4$: C, 71·98; H, 6·71; OMe, 41·3%).

The IR spectrum (Nujol^{R}) had peaks at 1600 (w), 1260 (s), 1075 (s), 1000 (s), 930 (s), 775 (s), 755 (m) cm^{-1}. The NMR spectrum ($CDCl_3$) showed relative areas of OMe to aromatic hydrogens of 1·5:1 in agreement with the structure. The diketal 9 (0·194 g, 0·000645 mole) was hydrolyzed in 5 ml of hot 95% EtOH containing 2 drops of 5% HCl aq. The pale yellow ppt of anthraquinone was collected and dried in air to give 0·130 g (0·000625 mole, 95% yield), m.p. 284°. A mixed m.p. with an authentic sample of anthraquinone was not depressed, and the IR spectra were identical.

7. *Electrolysis of benzodioxane at* Pt

Benzodioxane was prepared by a modified procedure of Dobrowsky,[21] b.p. 102–106°/20 mm, n_D^{27} 1·5470. A soln of 13·6 g (0·100 mole) of benzodioxane was electrolyzed in 250 ml MeOH containing 2 g KOH at 20° at 3·0 A for

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*In the first crystallization a mixture of plates and large colorless cubes precipitated. This mixture was separated by hand to give 6·0 g of cubic crystals, mp 145–155°, and 5·3 g of the plates, m.p. 157–174°. Recrystallization of the plates from 95% ethanol provided 5·0 g (0·021 mole; 42% yield) of recovered 9,10-dimethoxyanthracene, m.p. 202°.

5 hr. The crude product (16 g) was twice distilled to give 6·1 g (0·031 mole, 31% yield) of *trans*-**10**,[16] b.p. 102–106°/1·5 mm, n_D^{26} 1·4990. A higher boiling fraction 110–145°/1·5 mm was not examined further. The diketal **10** crystallized on standing for 1 day. This was recrystallized from water and then sublimed to give large colorless crystals, m.p. 88·5–89·5°. (Found: C, 60·37; H, 6·89; OMe, 30·72, Calc. for $C_{10}H_{14}O_4$: C, 60·59; H, 7·12; OMe, 31·31%).

The UV spectrum in EtOH exhibited absorption maxima at 225 nm ($\epsilon = 2900$) and 265 nm ($\epsilon = 2800$). The IR spectrum ($HCCl_3$) had peaks at 3050 (m), 2960 (m), 2880 (w), 1580 (w), 1395 (m), 1190 (m), 1160 (s), 1120 (m), 1100 (s), 1060 (s), 1040 (s), 1030 (s), 925 (s), 885 (m), 876 (m) cm^{-1}. Hydrolysis of 0·250 g (0·00125 mole) of **10** was carried out in 10 ml of water by addition of 1 g of Zn dust followed by 5 ml of HCl aq. After 5 min, the mixture was filtered and the filtrate extracted with ether. From the organic extract was isolated 0·100 g (0·0944 mole, 75·5% yield) of pyrocatechol, m.p. 104°. A mixed m.p. with an authentic sample of pyrocatechol was not depressed and the IR spectra were identical.

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