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An electrochemical route to trimethylhydroquinone

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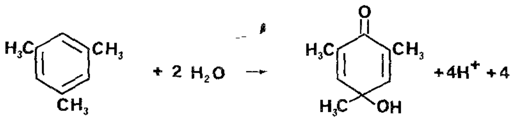
A new process for the synthesis of trimethylhydroquinone from mesitylene is presented. It consists of two steps, the first being the electrochemical oxidation of mesitylene to 2,4,6-trimethyl-4-hydroxycyclohexa-2,5-dien-1-one. In the second step this intermediate is chemically rearranged to trimethylhydroquinone. The overall yields were maximally 57% (material) and 40% (current) with 71% conversion. The electrochemical step is described and discussed in detail, while only preliminary results are presented for the chemical rearrangement.

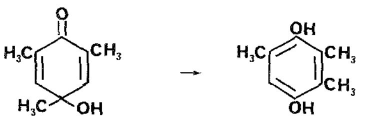
1. Introduction

Trimethylhydroquinone (TMHQ) is an important intermediate for the synthesis of vitamin E. Several methods have been devised for its production from 2,3,6-trimethylphenol or from pseudocumene [1–3]. They consist of two steps: oxidation of the starting material (by chemical or electrochemical means) to trimethylbenzoquinone (TMBQ) and subsequent catalytic reduction of TMBQ to TMHQ. Very good selectivity and conversion are obtained from the phenols, which however are expensive chemicals. On the other hand with pseudocumene, which is a cheap raw material, conversion must be kept very low (23%) in order to obtain acceptable selectivities (45%) [1]. An alternate route to TMHQ consists of chemical [4–11] or electrochemical [12, 13] oxidation of 2,4,6-trimethylphenol (mesitol) to 2,4,6-trimethyl-4-hydroxycyclohexa-2,5-dien-1-one (THCD), which can be converted to TMHQ through the well-known dienone-phenol base catalysed rearrangement [4, 14–25]. The problem with this process lies in the production of mesitol, for which the reported industrial method [4] consists of the tris-methylation of phenol and probably becomes economical just when mesitol is recovered with proper recycling in a plant aimed at the production of cresols.

Starting from these premises, we investigated a new process for the synthesis of TMHQ which starts from a cheap material; this is the electrochemical oxidation of mesitylene to THCD and its subsequent rearrangement to TMHQ (see Equations 1 and 2):



(1)



(2)

The idea of directly oxidizing an aromatic hydrocarbon with the aim of obtaining the same product as from the corresponding phenol should not be considered of general validity. The reason why it works on mesitylene is probably related to the peculiar unpaired spin density distribution in its cation radical, which exhibits unusually high values (and hence higher reactivity toward nucleophilic attack) at the ring positions [26]. This is the generally accepted explanation for a number of reactions of mesitylene involving a remarkably high nuclear to side-chain reactivity ratio. Examples are electrochemical [27] and chemical [27, 28] acetoxylation and biaryl-type oxidative coupling [29–32]. The

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purpose of our work was to study the industrial feasibility of the synthesis of TMHQ from mesitylene according to Reactions 1 and 2. The novel part of the process (the electrochemical step, Reaction 1 was studied in more detail and is described in the present paper. The rearrangement step (Reaction 2) was just adapted to our needs from literature data [15, 16] and only preliminary results on this reaction are reported here.

No actual optimization of the numerous variables involved in the two steps was carried out; however, some efforts were made to simplify the process as a whole as much as possible. In particular, the possibility of carrying out the rearrangement step (Reaction 2) without physical separation of the intermediate THCD from the reaction mixture was preliminarily explored, since it involved, in principle, only one purification step after the recovery of the final product TMHQ.

2. Experimental procedure

2.1. *Materials*

All chemicals and solvents except THCD and 3,5-dimethylbenzaldehyde (DMBA) were commercial, reagent grade products. THCD was first prepared by electrochemical oxidation of mesitol [12] for identification purposes. DMBA was obtained by oxidation of 3,5-dimethylbenzyl alcohol with $K_2Cr_2O_7$ [33].

2.2. *Electrochemical equipment and procedures*

Preliminary work was carried out with a simple small filter press cell (SFP cell). It consisted of two polypropylene frames and two plate electrodes ($100\,cm^2$ area each), with Viton as gasket material. Scale-up experiments were performed using the commercially available SU Electro Syn cell (ES cell) [34] in a configuration consisting of one anode working on both faces ($400 + 400\,cm^2$) and two single-faced cathodes ($400\,cm^2$ each). Frames and gaskets were of the same material as for the SFP cell. Both cells were equipped with a suitably placed reference electrode and Nafion 425 cationic membranes. As anode materials either graphite (Ellor, Le Carbone Lorrain) or lead dioxide deposited [35] on Pb–1% Ag alloy were used; cathodes were stainless steel. After each run the anode was washed with distilled water and stored dry. Best performance and reproducibility were obtained after several runs. Each experimental set-up consisted of the cell (SFP or ES), two resevoirs (300 ml or 5 litres), two heat exchangers and two centrifugal pumps (Iwaki MD 15 or MD 100). In the case of the ES cell, flow adjusting and measuring devices were also included. All materials contacted by the electrolytes were chosen to be as inert as possible: glass, Teflon, polypropylene and Viton. Power supplies were Amel 555B (10 A maximum) or Hewlett-Packard 6477C (50 A maximum), as required.

As the anodic solution exhibited a low electrical conductivity, electrode potentials at constant current were measured by the current interruption method [36]. For this purpose, an Amel 621 electrometer and an Amel 862/A XY recorder were used.

Polarization curves were obtained by plotting the electrode potentials measured at various currents in the SFP cell operated at the same temperature and flow as during real electrolyses.

Both with the SFP and the ES cells electrolyses were performed batchwise at constant current, recirculating the solutions though the cell until the desired amount of charge had been passed. While a single, initial amount of mesitylene was used with the SFP cell, periodic additions of the substrates (mesitylene and water) were performed with the ES cell: in this way more mesitylene can be electrolysed in a single batch.

2.3. *2,4,6-trimethyl-4-hydroxycyclohexa-2,5-dien-1-one* (*THCD*)

2.3.1. Analytical experiments. At the end of analytical experiments, the reaction mixture was worked-up and analysed by gas liquid chromatography (glc). All the anodic solution and the washings (2 × 300 ml of the same ACN/H_2O mixture used for the electrolysis) were collected together. A weighed amount of biphenyl (internal standard) was added to the solution or to a portion of it; 2 ml were withdrawn, diluted with an equal volume of water and extracted with ether (2 × 10 ml). The organic phase was filtered through a Whatman 1PS filter, dried on $MgSO_4$ and analysed on a Perkin Elmer Sigma 2 gas chromatograph equipped with a Hewlett-Packard 3388 integrator. The column was a SP 2100 (20% Supelcoport 100 to 120 mesh), 3 m long and 1/4 inch diameter in glass; temperature programming was 80 to 170° C at 3° C min^{-1} and then 170 to 240° C at 14° C min^{-1}. Quantitative analysis was calibrated with mixtures made up with authentic components.

2.3.2. Preparative experiments. In preparative runs, the anodic solution was set to pH 4 by adding 50% NaOH dropwise under stirring. The solution formed two phases, which were evaporated in a rotary evaporator at 40° C under reduced pressure until some water distilled. The distillate was worked-up and analysed by glc as described above. The residue (a biphasic mixture) was extracted with ether (4 × 1 volumes), the organic phase was dried with $MgSO_4$, filtered and evaporated. A red-yellow oil was obtained (about 50% in THCD), which was distilled using a Buchi Kugelrohr apparatus at 0.2 torr and 120 to 140° C. The yellow distillate (about 82% pure, named 'crude' THCD) was further purified by crystallization from pentane at −18° C. The white crystals (m.p. 44° C) were pure THCD according to ^{1}H-NMR and mass spectrometry (MS). In a crystallization experiment, 10 g of crude product gave 5.88 g THCD (purity 99%). The crystallization yield, based on the THCD content, was 71%.

2.4. *Trimethylhydroquinone (TMHQ)*

Instead of rearrangement of pure THCD in a second step [21, 22], we found that it can be performed without isolation at the end of the electrochemical step. A portion of the anodic solution was analysed as described in Section 2.3.1. The remaining part was set to pH 4 as above. The solution formed two phases which were distilled in a jacketed reactor equipped with bottom drain and motor stirrer at reduced pressure at 40° C, leaving as residue a heterogeneous mixture containing essentially THCD, heavy molecular weight by-products and water. The volume of the solution was adjusted to a THCD concentration of about 20 g l^{-1}. Under nitrogen atmosphere, sodium metabisulphite (1 g l^{-1}) and sodium hydroxide (40 g l^{-1}) were added. The mixture was allowed to react with stirring under nitrogen for 1 h at 95° C. After cooling at room temperature, the stoichiometric amount of H_2SO_4 (as 20% aqueous solution) was added. The mixture was extracted with one volume of methylisobutylketone. The organic phase was filtered, completely evaporated in a rotary evaporator and dried under vacuum. Crude TMHQ was dissolved in boiling octane (60 ml g^{-1}) and the hot mixture was filtered. TMHQ crystallized at room temperature as a brown solid, the identity of which was confirmed by ^{1}H-NMR and MS. Quantitative analysis of TMHQ was performed with the same column used for THCD at 150° C using hydroquinone dimethylether as internal standard.

3. Results and discussion

3.1. *2,4,6-trimethyl-4-hydroxycyclohexa-2,5-dien-1-one (THCD)*

3.1.1. Preliminary results. Mesitylene is reported to undergo anodic oxidation in strongly acidic media [37–40] yielding 3,5-dimethylbenzaldehyde as the main product. An interesting piece of information is however contained in one paper [38], i.e. the mentioning of mesitol being present in the reaction mixture. As this compound is known to be oxidizable to THCD [12], we carried out the anodic oxidation of mesitylene in similar conditions, i.e. in a divided cell with lead anode and ACN–H_2O–H_2SO_4 as the electrolyte: THCD was found to be the main product, stimulating therefore further experimentation. However, as lead gave irreproducible results under our reaction conditions, a more reliable electrode was looked for.

3.1.2. Analytical experiments (SFP cell). Table 1 shows the results of two sets of repeated experiments, the first at a graphite and the other at a PbO_2/Pb–1%Ag anode.

Heavy molecular weight compounds and oxygen (Rows h and i) were not determined directly, but approximately estimated as follows. Using ^{1}H-NMR and MS, no other low molecular

Table 1.

	Graphite anode[1]			PbO_2/Pb–1% Ag anode[2]			PbO_2/Pb–1% Ag anode[3]		
	Conversion (%)	*Selectivity* (%)	*Current Yield* (%)	*Conversion* (%)	*Selectivity* (%)	*Current Yield* (%)	*Conversion* (%)	*Selectivity* (%)	*Current Yield* (%)
(a) Mesitylene[4]	50.2	–	–	46.4	–	–	71.1	–	–
(b) 2,6-dimethylbenzoquinone[4]	–	2.9	4.4	–	2.4	3.3	–	4.0	4.3
(c) 3,5-dimethylbenzaldehyde[4]	–	6.2	6.3	–	7.9	7.2	–	10.6	7.5
(d) Mesitol[4]	–	0.0	0.0	–	1.5	0.7	–	0.6	0.2
(e) THCD[4]	–	47.3	47.5	–	49.2	45.3	–	56.7	40.3
(f) 3,5-dimethylbenzylalcohol[4]	–	1.1	0.6	–	4.8	2.2	–	3.0	1.0
(g) 2,4,6-trimethylbenzaldehyde[4]	–	0.3	0.3	–	0.0	0.0	–	0.1	0.1
(h) Heavy compounds[5]	–	42.2	21.0	–	34.2	15.7	–	25.1	9.0
(i) Oxygen[5]	–	–	19.9	–	–	25.6	–	–	37.6

[1] SFP cell; current, $i = 7\,\mathrm{mA\,cm^{-2}}$; temperature, $t = 8°\mathrm{C}$; charge, $Q = 2\mathrm{F\,mol^{-1}}$; anodic solution: 200 ml H_2O + 800 ml ACN + 5 ml H_2SO_4 (96%) + 10 ml mesitylene; cathodic solution: 1000 ml H_2O + 5 ml H_2SO_4 (96%); results are averages of three runs.

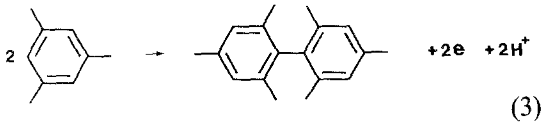
[2] SFP cell; $i = 16\,\mathrm{mA\,cm^{-2}}$; $t = 18°\mathrm{C}$; $Q = 2\mathrm{F\,mol^{-1}}$; anodic solution: 200 ml H_2O + 800 ml ACN + 10 ml H_2SO_4 (96%) + 10 ml mesitylene; cathodic solution: 1000 ml H_2O + 10 ml H_2SO_4 (96%); results are averages of eight runs.

[3] ES cell; $i = 35\,\mathrm{mA\,cm^{-2}}$; $t = 30°\mathrm{C}$; $Q = 4\mathrm{F\,mol^{-1}}$. Anodic solution: 1 litre H_2O + 4 litre ACN + 50 ml H_2SO_4 (96%); 300 ml mesitylene and 78 ml H_2O were added in five portions during the run. Cathodic solution: 5 litre H_2O + 50 ml H_2SO_4 (96%). Results are averages of four runs.

[4] Determined by glc.

[5] Estimated (see text).

weight compounds (e.g. carboxylic acids) were detected in appreciable amounts, so it can be inferred that all the mesitylene consumed and not accounted for by the glc analysis of the solution at the end of the run reacts to give high molecular weight compounds. The selectivity in Row h of Table 1 is therefore simply obtained as the difference from 100%. In order to also estimate current yield for heavy compounds, these are supposed to be diphenyl-type oligomers and polymers [29–32]. The formation of a dimer needs two electrons, as shown in Equation 3.



(3)

Analogously, in the formation of the n-th order polymer, $2(n - 1)$ electrons are consumed. Supposing that n is large enough, $2(n - 1)$ approximates to $2n$, i.e. for each molecule of mesitylene involved in the formation of high molecular weight compounds, two electrons are consumed. According to this approximation current yields shown in Row h of Table 1 were calculated. Finally, the difference from 100% total current yield is assigned to oxygen evolution (Row i). Table 1 shows a remarkable similarity between the electrochemical reactions carried out on graphite and on PbO_2/Pb–1% Ag, even if there are differences in the experimental conditions. Although this can be reasonably assumed as a piece of evidence against a 'chemical' participation of the PbO_2 electrode, more work is needed to solve this recurring problem [12]. We used this fact to our advantage to perform some preliminary investigations on graphite which, although not suitable for industrial work in the presence of sulphuric acid [41], gave reproducible results for a reasonable number of runs and, furthermore, was cheap enough to be discarded frequently.

Among the by-products listed in Table 1 the compounds in Rows c, d, f and h are the ones expected from side-chain or aromatic ring oxidation of mesitylene. The formation of the compounds listed in Rows b (with one carbon atom less than the starting material) and g (with one carbon atom more than the starting material) was not investigated; however it should be noted that 2,6-dimethylbenzoquinone is also found in the anodic oxidation of mesitol [12].

3.1.3. Preparative experiments (SFP cell). Preparative experiments carried out under the same conditions as those reported in Table 1 on graphite and on PbO_2/Pb–1%Ag confirmed the similarity in the behaviour of these electrodes. A typical preparation with graphite as the anode, starting from 10 ml (8.64 g) of mesitylene, gave 2.91 g of crude THCD (purity 82%) and 0.87 g of high molecular weight compounds, while 4.47 g of unreacted mesitylene were determined in the reaction mixture. Analogously, on PbO_2/Pb–1%Ag 3.25 g of crude THCD (83% purity), 0.53 g high molecular weight compounds and 4.23 g of unreacted mesitylene were obtained. Conversions, selectivities and current yields obtained in these experiments are reported in Table 2.

Furthermore, a comparison of the data of Tables 1 and 2 shows that THCD determined by glc in the reaction mixture can be almost quantitatively recovered, if needed. These experiments also served to select the electrode best suited for industrial use: this was the PbO_2/Pb–1%Ag anode, due especially to its stability to corrosion. All further work was therefore based on this electrode.

3.1.4. Polarization curves (SFP cell). Fig. 1 shows polarization curves of the supporting electrolyte compared with those of mesitylene and THCD.

It is noted that addition of mesitylene depolarizes the anode; furthermore, this effect is proportional to the concentration of mesitylene. On the other hand, the presence of THCD shifts the curve in the anodic direction. The effect of

*Table 2**

Anode	*Mesitylene conversion* (%)	*THCD*	
		Selectivity (%)	*Current yield* (%)
Graphite	48	45	43
PbO_2/Pb–1%Ag	51	48	49

* For experimental details see footnotes 1 and 2 of Table 1.

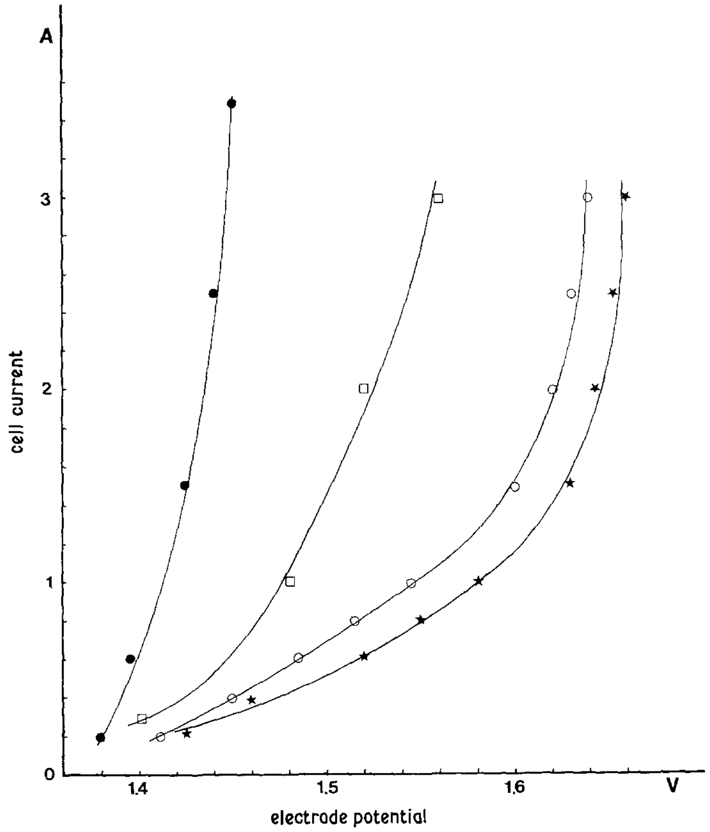


Fig. 1. Polarization curves for the system mesitylene–ACN–H_2O–H_2SO_4 at 30° C: cell current (A) versus electrode potential (V versus SCE). (○) Supporting electrolyte; (●) supporting electrolyte plus 0.14 M mesitylene; (□) supporting electrolyte plus 0.014 M mesitylene; (★) supporting electrolyte plus 0.016 M THCD.

the concentration of mesitylene is even more apparent in the semilogarithmic plot shown in Fig. 2.

From these data it can be concluded that during the electrolysis the electrode potential will rise due to consumption of mesitylene and formation of THCD. This can be corrected for by means of periodical additions of mesitylene to the anodic solution. In practice, working with an initial concentration of mesitylene 0.14 M and a cell current of 1 to 2.5 A the electrode potential ranges from 1.41 to 1.44 V versus SCE. When the concentration of mesitylene, for example, is tenfold less the potential rises to 1.48 to 1.54 V versus SCE for the current range mentioned above. It must be stressed that these polarization curves were obtained with the SFP cell, but the trends observed were nevertheless found useful as a guide for scale-up experiments.

3.1.5. Scale-up experiments (*ES cell*). It was found that the reaction can be scaled-up from the SFP to the ES cell essentially without changes; however, due to the better performance of the large cell, a higher current density, a higher temperature and a higher mesitylene concentration and conversion could be used without gross worsening of the current yield. Table 1 shows the results.

A mean value of 1.50 V versus SCE for the electrode potential was obtained at the end of the runs; variations during the experiments were less than 0.05 V. The cell voltage was 4.0 V.

Large scale runs indicated a phenomenon that was not clearly apparent from the small scale work, i.e. transfer of the solvents (both H_2O and ACN) from the anodic to the cathodic compartment of the cell through the membrane.

The situation is probably a complex one, arising from two different effects. The first effect (which is operative also in the absence of electrical current) is solvent interdiffusion. A second effect, overlapping the first one in the presence of a current is the well known water transfer [42], probably as solvation molecules in H^+ electromigration. No attempt was made to separate

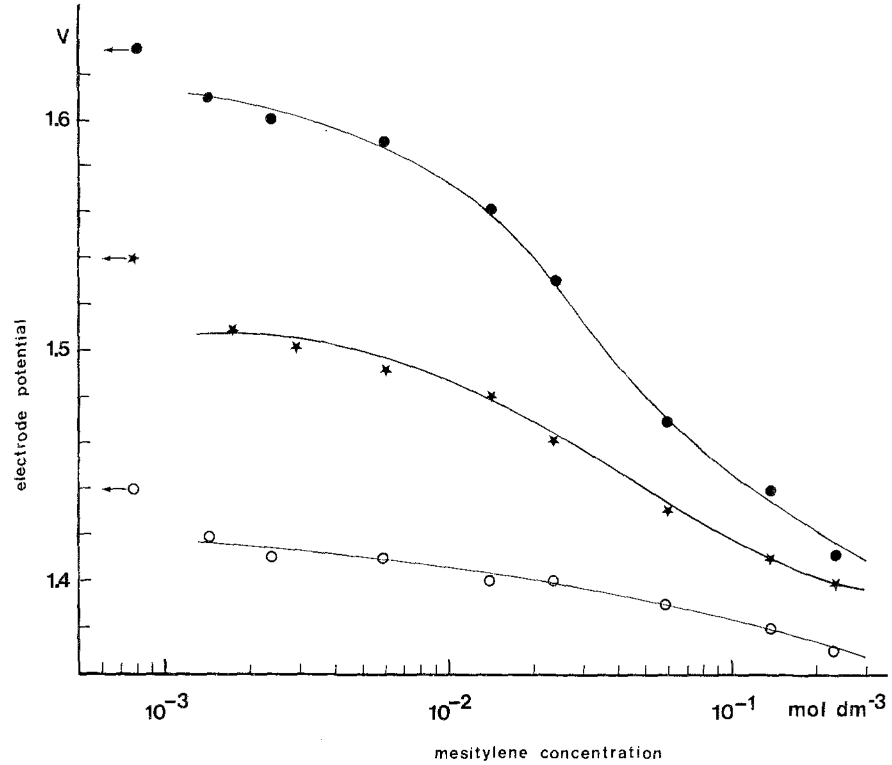


Fig. 2. Electrode potential (V versus SCE) as a function of mesitylene concentration (mol dm^{-3}). (○) 0.3 A cell current; (★) 1 A cell current; (●) 3 A cell current. Arrows on the vertical axis indicate potentials of basic curves (supporting electrolyte only).

those two components. Control experiments showed that at the end of the electrolysis about 570 g H_2O and 290 g ACN were transferred from anolyte to catholyte under our experimental conditions (averages of two runs).

From Table 1, relevant data for the electrosynthesis of THCD from mesitylene can be extracted:

Conversion	71%
Selectivity	57%
Current yield	40%
Cell voltage	4 V
Current density	35 mA cm^{-2}

From these data an energy consumption E = 7 kWh kg^{-1} (based on product weight) can be calculated, which compares well with other industrial electro-organic processes [43].

3.2. *Trimethylhydroquinone*

The procedures reported by Bamberger and Rising [15] and by Sato *et al.* [16] are very similar. We used a slightly modified method (see section 2) and found that it was possible to work both with pure (99%) or crude (82%) THCD, obtaining essentially the same results reported in the cited literature. This prompted us to a preliminary study of the rearrangement of THCD to TMHQ without physically separating it from the reaction mixture.

Isomerization of the non-isolated THCD as described yielded 74% selectivity and 100% conversion, i.e. essentially the same figures as reported in the literature for the pure THCD [15, 16]. Crude TMHQ was of about 50% purity. Purification by one crystallization from boiling octane gives TMHQ with 80 to 85% purity in 90 to 100% yield.

4. Conclusions

1. We have shown that mesitylene, a cheap starting material, can be electrochemically oxidized to THCD with reasonable efficiency.

2. This electrochemical reaction can form the first step of a new route to TMHQ.
3. The second step of the process, the chemical rearrangement of THCD to TMHQ, which is a well-known reaction, can be performed without isolation of THCD from the electrochemical reaction mixture.

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