

## Studies on Electrolytic Substitution Reactions

VI.<sup>1</sup> On the Mechanism of Anodic Acetamidation\*

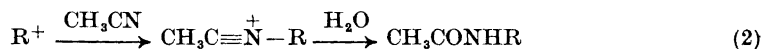
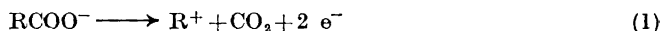
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Anodic oxidation of a methylsubstituted aromatic hydrocarbon at a platinum anode in nominally anhydrous acetonitrile with sodium perchlorate or tetrabutylammonium tetrafluoroborate as supporting electrolyte gives a mixture of an *N*-benzylacetamide and the corresponding benzyl alcohol and benzaldehyde, together with small amounts of coupling products (bibenzyls and/or diphenylmethanes). The acetamide is the predominant product in anhydrous medium; on addition of water the yield of alcohol and aldehyde increases. Optimal yields of acetamide were obtained at the carbon anode, where the presence of small amounts of water in the nominally anhydrous medium has no deleterious effect.

A mechanism involving formation of a cation radical as the initial step is proposed. This produces a benzyl radical by proton loss and the radical is then oxidized in a second step to give a benzyl cation. The reactivity order of anodically generated cations toward water and acetonitrile appears to be the reverse of that observed in homogeneous carbonium ion processes, in that the *more stable* cations are more selective toward the *weaker* nucleophile, acetonitrile, in the anodic process.

Some years ago we reported<sup>2</sup> that cations generated by anodic oxidation<sup>2a</sup> of carboxylates<sup>3</sup> could be trapped by acetonitrile in a Ritter-type reaction. The final product was an *N*-alkylacetamide (eqns. 1 and 2):



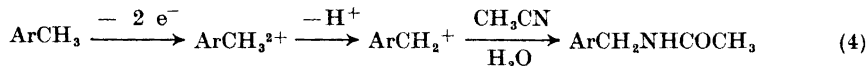
Later, in a preliminary communication,<sup>4</sup> it was demonstrated that anodic oxidation of durene and hexamethylbenzene in acetonitrile/sodium perchlorate at a platinum anode led to the formation of substituted *N*-benzylacetamides

\* This work was presented in part at the Symposium on Synthetic and Mechanistic Aspects of Electroorganic Chemistry, US Army Research Office-Durham, N.C., October 1968.

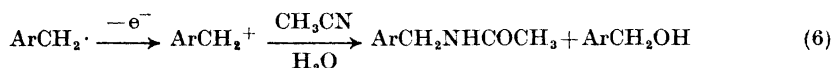
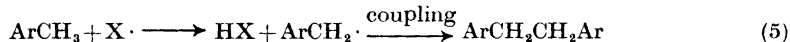
(eqn. 3). Since these reactions could be performed at anode potentials considerably lower than that required for oxidation of acetonitrile/sodium



perchlorate alone, it was suggested that the aromatic substrate was the electroactive species, being oxidized to a benzylic cation *via* a dicationic intermediate (eqn. 4). Addition of 3 % of water to the electrolyte gave the corresponding benzyl alcohol as an additional product.



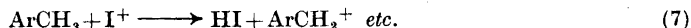
Parker and Burgert<sup>5</sup> have criticized this interpretation on the following grounds: Anodic oxidation of toluene, acetonitrile (5.5 M in water) and a perchlorate (lithium, sodium, or tetrapropylammonium perchlorate) produced bibenzyl, *N*-benzylacetamide (predominantly), benzyl alcohol, benzaldehyde, and benzoic acid. The electrolyses were normally run at 2.7 V *vs.* the SCE, but similar product mixtures were also obtained in the interval 1.6–2.4 V. In the absence of water, *N*-benzylacetamide was the sole product. Clearly bibenzyl can only be formed in a radical coupling reaction between two benzyl radicals, so the benzyl radical must be an intermediate. Since toluene has a half-wave potential of 2.3 V *vs.* the SCE in this system,<sup>6</sup> it was concluded that the initial step could not be the direct oxidation of the substrate. Instead, a radical X· (not defined, but assumed to be produced by oxidation of water or perchlorate ion), would abstract a hydrogen atom from the side-chain of the substrate to form a benzyl radical. This might undergo coupling in the bulk of the solution or be further oxidized at the anode to form a benzyl cation (eqns. 5 and 6). In the presence of water, which is very difficult to remove completely from this system, the benzyl cation is diverted between *N*-benzylacetamide and benzyl alcohol formation.



Benzaldehyde and benzoic acid are formed by further oxidation of benzyl alcohol.

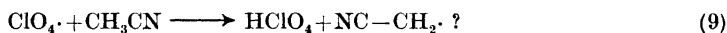
Similar views have been expressed for other side-chain substitution reactions at the anode, such as methoxylation,<sup>7</sup> substitution by cyanate ion,<sup>8</sup> and acetoxylation<sup>9</sup> in the medium acetic acid/tetramethylammonium nitrate.

In a study of anodically initiated iodination of aromatic compounds by electrolysis in a medium consisting of acetonitrile/iodine/lithium perchlorate Miller<sup>10</sup> also observed side-chain acetamidation of *p*-xylene and triphenylmethane (but not toluene and mesitylene). A mechanism (eqn. 7) involving hydride ion abstraction from the side-chain by an anodically generated positive iodine species was suggested:



Acetonitrile/perchlorate is widely regarded as a very good medium for anodic voltammetry because of its high resistance towards anodic oxidation. Anhydrous 0.5 M sodium perchlorate in acetonitrile is not attacked anodically until a potential of about 2.2 V *vs.* the Ag/0.1 M Ag<sup>+</sup> electrode<sup>6,11</sup> is reached. (Unless otherwise stated, all electrode potentials mentioned in this report will be given with this electrode as reference.) Billon<sup>12,13</sup> puts the anodic limit of 0.1 M sodium or tetrabutylammonium perchlorate at about 2.3 V and has also demonstrated that addition of up to 6 % of water to the electrolyte only changes the voltammetric curve by a very small extent. Thus, polarographic studies at the rotating platinum anode<sup>6,11,14-16</sup> of substrates as difficult to oxidize as benzene ( $E_3 = 2.0$  V) are possible in this medium.

The anode reaction in acetonitrile/perchlorate was first assumed to be the discharge of the perchlorate ion<sup>17</sup> with formation of the perchlorate radical, followed by reaction with acetonitrile to form the cyanomethyl radical (eqns. 8 and 9). It was claimed that the cyanomethyl radicals ended up as succinonitrile,<sup>17</sup> but later work<sup>12,13,18</sup> has failed to confirm this result. Billon<sup>12,13</sup> found that products with retention times considerably longer than that of acetonitrile were formed, but the nature of these products was not investigated.



ESR studies<sup>13,19</sup> on the anodic oxidation of perchlorate ion in acetonitrile were originally taken as supporting evidence for the intermediacy of perchlorate radicals. However, it has later been shown that the ESR spectrum obtained is identical to that of chlorine dioxide.<sup>20</sup>

From the data available, one can conclude that acetonitrile/perchlorate is very resistant towards oxidation at the platinum anode, the reaction taking place at an appreciable rate only at potentials above 2.3 V. The nature of the electrode process still appears to be unknown.

We have now repeated and extended our studies on the side-chain acetamidation reaction. The results, to be presented below, clearly demonstrate that the initial step is the direct anodic oxidation of the aromatic substrate. A remarkable feature of the reaction is that the nucleophilicity order between acetonitrile and water towards anodically generated benzyl cations appears to be the reverse one as compared to analogous reactions in homogeneous media.

## RESULTS

We have confirmed some of the above-mentioned results for anodic oxidation of acetonitrile/anhydrous 0.5 M sodium perchlorate at a platinum anode. Under our actual electrolytic conditions (anode area about 50 cm<sup>2</sup>, Ag/0.1 M Ag<sup>+</sup> in acetonitrile as a reference electrode), the voltammetric curve starts to rise sharply at about 2.4 V (see Fig. 1). Experiments designed to study the product spectrum from the background reaction (run at 2.7 V) are only at a preliminary stage at present, but we have been able to confirm that succinonitrile is not formed. At least six other compounds with considerably longer

retention times than acetonitrile are formed. The masses of the molecular ions in their mass spectra (118, 147, 157, 171, and 210, respectively) suggest that two or more acetonitrile molecules must be involved in their formation, but since these preliminary experiments were run in an undivided cell we do not wish to speculate about their possible structure at present. The cathode reaction cannot be excluded as a source of at least some of these compounds.<sup>12,13</sup>

The addition of alkylaromatic substrates (concentration = 0.20 M) to the acetonitrile/sodium perchlorate medium brings about profound changes in the voltammetric curve. Fig. 1 shows the voltammetric curves for toluene,

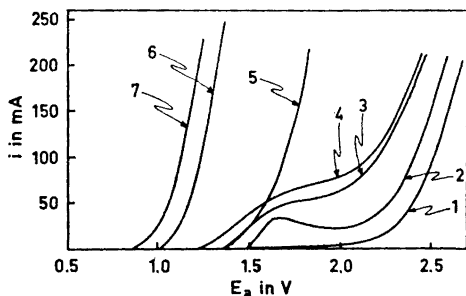


Fig. 1. Anodic voltammetry of alkylaromatic compounds (0.20 M) in anhydrous acetonitrile/0.5 M sodium perchlorate at a Pt anode (area 50 cm<sup>2</sup>). 1=background, 2=toluene, 3=*m*-xylene, 4=*p*-xylene, 5=*o*-xylene, 6=durene, and 7=hexamethylbenzene.

the xylenes, durene, and hexamethylbenzene. In all cases a new anodic process at considerably lower potential than that required for the background reaction takes place. This shows that the substrate is directly involved in an anodic oxidation process; preparative experiments at controlled potentials, chosen with the guidance of the curves of Fig. 1, unequivocally show that this oxidation process is linked with side-chain acetamidation.

Product isolation and analysis were carried out after 10 % conversion (as calculated for a two-electron process) in order to avoid complications due to secondary oxidation reactions.<sup>20</sup> At this conversion level it was possible to avoid further oxidation of the aldehyde to the corresponding benzoic acid,<sup>5</sup> as was established in separate experiments in which the product mixture was treated with a slight excess of diazomethane in order to convert any carboxylic acid formed to its methyl ester. Analyses of these reaction mixtures showed that carboxylic acid formation was negligible.

Table 1 gives product distributions for anodic oxidation of the above-mentioned hydrocarbons in nominally anhydrous acetonitrile/0.5 M sodium perchlorate. This term designates a medium made up from anhydrous sodium perchlorate and analytical grade acetonitrile without any special precautions to remove traces of water or exclude moisture from the air. The predominant product in all cases is the *N*-benzylacetamide, accompanied by small amounts of the alcohol, aldehyde, and bibenzyl derivative. In some cases we noted that small amounts of substituted diphenylmethanes were formed; this reaction was also observed during the anodic oxidation of cumene in the same medium.<sup>18</sup>

The results given in Table 1 refer to a nominally anhydrous electrolyte, the water content of which generally is about 0.1 M. Tables 2 and 3 show how

Table 1. Product distributions in the anodic oxidation of alkylaromatic compounds (0.20 M) in acetonitrile/0.5 M sodium perchlorate (nominally anhydrous<sup>a</sup>).

Substrate, ArCH <sub>3</sub>	Anode potential	Current yield <sup>b</sup>	ArCHO	Relative product distribution			
				ArCH <sub>2</sub> OH	ArCH <sub>2</sub> NHCOCH <sub>3</sub>	ArCH <sub>2</sub> CH <sub>2</sub> Ar	ArCH <sub>2</sub> Ar'CH <sub>3</sub>
Toluene	1.85	37	20	10	62	8	—
<i>o</i> -Xylene	1.70	41	9	5	82	1	3 <sup>c</sup>
<i>m</i> -Xylene	1.80	36	16	8	68	2	6 <sup>d</sup>
<i>p</i> -Xylene	1.70	41	8	4	71	17	—
Durene	1.20	53	6	—	68	—	26 <sup>e</sup>
Hexamethylbenzene	1.00	70	—	—	100	—	—

<sup>a</sup> [H<sub>2</sub>O]=0.1 M. <sup>b</sup> Calculated for a two-electron process.

<sup>c</sup> 4-(2-Methylbenzyl)-1,2-dimethylbenzene. <sup>d</sup> 4-(3-Methylbenzyl)-1,3-dimethylbenzene.

<sup>e</sup> 3-(2,4,5-Trimethylbenzyl)-1,2,4,5-tetramethylbenzene. In this case the product distribution was poorly reproducible; relative yields of up to 75 % of the diphenylmethane derivative were sometimes observed. We have as yet no explanation for this behavior.

Table 2. Product distribution in the anodic oxidation of *o*-xylene (0.20 M) in acetonitrile/0.5 M sodium perchlorate in the presence of water. Anode potential=1.7 V.

[H <sub>2</sub> O], %	Relative product distribution				
	ArCHO	ArCH <sub>2</sub> OH	ArCH <sub>2</sub> NHCOCH <sub>3</sub>	ArCH <sub>2</sub> CH <sub>2</sub> Ar	ArCH <sub>2</sub> Ar'CH <sub>3</sub> <sup>a</sup>
Anhydrous <sup>b</sup>	6	4	89	—	1
Anhydrous <sup>c</sup>	9	5	82	1	3
0.5	10	12	76	2	1
1	10	14	72	2	2
2	10	15	72	1	3
3	11	21	65	—	3
4	10	16	72	—	2
5	28	27	43	—	2

<sup>a</sup> See Table 1. <sup>b</sup> The electrolyte was passed over molecular sieves (4A) before electrolysis.  
<sup>c</sup> [H<sub>2</sub>O]=0.1 M.

Table 3. Product distribution in the anodic oxidation of *p*-xylene (0.20 M) in acetonitrile/0.5 M sodium perchlorate in the presence of water. Anode potential=1.7 V.

[H <sub>2</sub> O], %	Relative product distribution			
	ArCHO	ArCH <sub>2</sub> OH	ArCH <sub>2</sub> NHCOCH <sub>3</sub>	ArCH <sub>2</sub> CH <sub>2</sub> Ar
Anhydrous <sup>a</sup>	5	2	84	9
Anhydrous <sup>b</sup>	8	4	71	17
0.5	23	10	55	11
1	37	15	41	7
2	37	27	33	4
3	35	27	35	4
4	29	32	37	3
5	28	32	38	2

<sup>a</sup> The electrolyte was passed over molecular sieves (4A) before electrolysis.  
<sup>b</sup> [H<sub>2</sub>O]=0.1 M.

the addition of increasing amounts of water to the electrolyte influences the product distribution from anodic oxidation of *o*- and *p*-xylene. Both aldehyde and alcohol yields increase in the presence of water at the expense of the *N*-benzylacetamide. Conversely, by passing the electrolyte over molecular sieves (4A) these yields could be further decreased; it is probably possible to further decrease the yields of these products by adopting more rigorous precautions to remove and exclude water.

Table 4 demonstrates the effect on the product distribution of adding water to the electrolyte from anodic oxidation of hexamethylbenzene. Here the change in product distribution is much less profound than for *o*- and *p*-xylene, the *N*-pentamethylbenzylacetamide still being the major product

at a water concentration of 5 %. This behavior is in variance with our preliminary observation <sup>4</sup> that addition of 3 % of water to the electrolyte led to the formation of predominantly pentamethylbenzyl alcohol. The data in Table 4 are reasonably well reproducible, so we have to conclude that our

Table 4. Product distribution in the anodic oxidation of hexamethylbenzene (0.04 M) in acetonitrile/0.5 M sodium perchlorate in the presence of water. Anode potential = 1.1 V.

[H <sub>2</sub> O], %	Relative product distribution		
	ArCHO	ArCH <sub>2</sub> OH	ArCH <sub>2</sub> NHCOCH <sub>3</sub>
Anhydrous <sup>a</sup>			100 <sup>b</sup>
0.5			100 <sup>b</sup>
1	0.3		99.7
2	1.0	2.6	96.4
3	1.8	4.4	93.8
4	1.5	3.8	94.7
5	3.3	5.7	91.0

<sup>a</sup> [H<sub>2</sub>O] = 0.1 M. <sup>b</sup> The limit for detection of ArCHO and ArCH<sub>2</sub>OH is about 0.1 %.

previous result in 3 % water/acetonitrile must be faulty due to an inadequate analytical procedure (not based on VPC).

Finally, Table 5 shows the effect of using a carbon anode instead of the usual platinum anode in the oxidation of *o*- and *p*-xylene. One can note that the carbon anode oxidations do not appear to be very sensitive towards the small water concentration in the nominally anhydrous solvent. This is of potential preparative value and the use of carbon anodes for large-scale acetamidations is currently being explored. In this connection it should be pointed out that the potentially dangerous use of sodium perchlorate as a supporting electrolyte in large-scale runs can be avoided by using tetrabutylammonium tetrafluoroborate. This compound gives almost identical results in the acetamidation process and is generally an excellent supporting electrolyte for anodic work since it has a very high anodic limit and is easily soluble in most organic solvents but almost completely insoluble in water.

In none of the electrolyses with an alkylaromatic substrate present were any of the products, obtained by oxidation of acetonitrile/sodium perchlorate alone, detectable on the VPC traces.

## DISCUSSION

As shown in Fig. 1 and supported by the available literature data, acetonitrile/sodium perchlorate is not attacked anodically at potentials below 2.4 V. On the other hand, voltammetric curves obtained from solutions containing alkylaromatic substrates clearly demonstrate that these hydrocarbons are involved in direct oxidation processes taking place at lower anode potentials.

Table 5. Comparison between C and Pt anodes in the anodic oxidation of *o*-, and *p*-xylene in acetomitrile/0.5 M sodium perchlorate. Anode potential = 1.7 V.

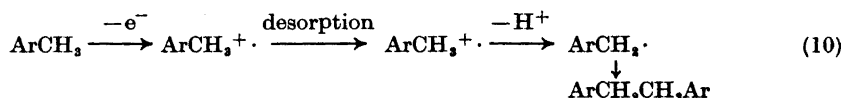
Substrate Ar-CH <sub>3</sub>	[H <sub>2</sub> O], %	Anode material	ArCHO	ArCH <sub>2</sub> OH	ArCH <sub>2</sub> NHCOCH <sub>3</sub>	ArCH <sub>2</sub> CH <sub>2</sub> Ar	ArCH <sub>2</sub> Ar'CH <sub>3</sub> <sup>b</sup>
<i>o</i> -Xylene	Anhydrous <sup>a</sup>	Pt	9	5	82	1	3
<i>o</i> -Xylene	2	Pt	10	15	72	1	3
<i>o</i> -Xylene	Anhydrous <sup>a</sup>	C	3	—	95	—	2
<i>o</i> -Xylene	2	C	11	7	82	—	—
<i>p</i> -Xylene	Anhydrous <sup>a</sup>	Pt	8	4	71	17	—
<i>p</i> -Xylene	2	Pt	37	27	33	4	—
<i>p</i> -Xylene	Anhydrous <sup>a</sup>	C	1	—	86	13	—
<i>p</i> -Xylene	2	C	20	7	70	3	—

<sup>a</sup> [H<sub>2</sub>O] = 0.1 M. <sup>b</sup> See Table 1.

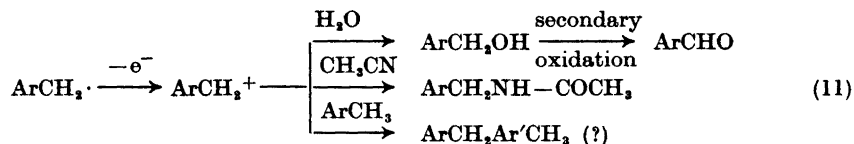


Controlled potential electrolyses (Tables 1–5) at potentials in the region 1.0–1.9 V, depending on the particular substrate employed, show that side-chain acetamidation and hydroxylation do occur under these conditions. In view of these facts, we still prefer a mechanism involving direct oxidation of the substrate, suitably modified to account for the formation of radical coupling product.

The first step would then be a one-electron oxidation to form a cation radical as the first intermediate (equation 10).<sup>22</sup> This can escape from the electrode surface and lose a proton to form a benzyl radical in the bulk of the solution; the benzyl radicals then combine to give bibenzyl:



If, however, the benzyl radical is formed by proton loss from a cation radical at the electrode surface or in its immediate vicinity, it will be further oxidized to a benzyl cation (eqn. 11) which gives rise to the benzyl alcohol, the *N*-benzylacetamide, and possibly, the diphenylmethane derivative. From its ionization potential the benzyl radical has been estimated to have a half-wave potential of less than 0.9 V, so this oxidation process will take place with great ease at the potentials employed in the electrolytic runs.



In our preliminary communication,<sup>4</sup> the preparative oxidations of durene and hexamethylbenzene were performed at 1.0 and 0.8 V *vs.* the SCE, respectively. These potentials seem to be unreasonably low and in view of the above results we have to conclude that they must have been in error, probably due to the fact that the SCE was used as a reference electrode. We have later observed that the SCE performs irregularly in acetonitrile and have therefore resorted to the much more reliable Ag/0.1 M Ag<sup>+</sup> electrode. This gives well reproducible results.

A very interesting picture emerges when one examines the competition between the two nucleophiles, acetonitrile and water, for reaction with anodically generated cations. From recent studies on the reaction between alkyl cations generated by oxidation of alkyl radicals by Cu(II) complexes, and a mixture of acetonitrile and acetic acid,<sup>23</sup> it can be concluded that these two reagents must be of comparable nucleophilicity in homogeneous media and therefore acetonitrile a much weaker nucleophile than water. It would therefore be expected that less stable cations, *e.g.* the benzyl cation, will be less selective towards a mixture of acetonitrile and water, whereas a more stable cation, such as the pentamethylbenzyl cation, will be more selective. This means that the reaction with the much stronger nucleophile, water, should be favored as the cation becomes more stable.<sup>24</sup>

Table 6. Log (yield of acetamide/yield of alcohol + aldehyde) for different substrates in the nominally anhydrous system.

Substrate	Log $\frac{\text{Yield of acetamide}}{\text{Yield of alcohol + aldehyde}}$
Toluene	0.32
<i>o</i> -Xylene	0.77
<i>m</i> -Xylene	0.45
<i>p</i> -Xylene	0.77
Durene	1.04
Hexamethylbenzene	> 3

In fact, the opposite behavior is observed for anodically generated cations as can be seen by inspection of Table 6. Here the logarithm of the ratio between the yield of acetamide and the combined yield of alcohol and aldehyde has been listed for the different substrates in Table 1. In these experiments, the water concentration is of the order of 0.1 M. The trend is indeed an increased selectivity as the cation becomes more stable, but *the selectivity is towards the weaker nucleophile*.

It is also instructive to treat the data of Tables 2–4 in the same manner and plot the values obtained against water concentration (Fig. 2). Truly, the

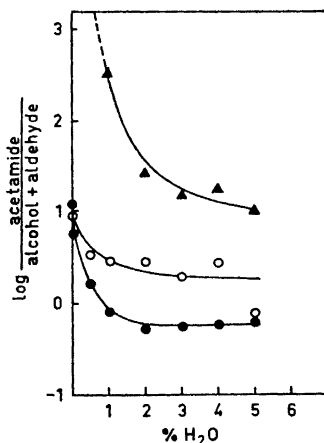


Fig. 2. Plot of  $\log \frac{\text{acetamide}}{\text{alcohol + aldehyde}}$  vs. percentage water in the electrolyte. Filled circles = *p*-xylene, open circles = *o*-xylene, and triangles = hexamethylbenzene (see also Tables 2–4).

ratio decreases as the water concentration increases, but at least for *o*- and *p*-xylene it reaches a plateau value between 2 and 5 % water. For hexamethylbenzene, a constant value is not reached in the experimentally accessible region (due to the insolubility of hexamethylbenzene, it is not possible to work at higher water concentrations).

We have as yet no consistent explanation for these phenomena, except that they clearly indicate that the bulk composition of the solvent does not

reflect the composition at the electrode and in its vicinity.\* Thus we have possibly here a case of a significant difference between an organic electrode process and an analogous homogeneous process, although opinion must be somewhat reserved until the relative nucleophilicities of acetonitrile and water in homogeneous media have been quantitatively established.

Finally, we wish to comment on Miller's interpretation of the acetamidation reaction (eqn. 7). We do not think it necessary to try to account for both aromatic iodination and side-chain acetamidation within a single mechanism involving iodo cations; instead two parallel reactions with distinctly different mechanisms may take place. It would be of great interest to have more information regarding anode potentials for these processes. Iodine is known to undergo an oxidation process<sup>2a</sup> at about 1.9 V, so if the positive iodine species is generated by this reaction the anode potential must also be high enough for direct oxidation of the substrate.

### EXPERIMENTAL

*Reagents and reference compounds.* Acetonitrile (Fluka AG, Buchs, Switzerland) was of analytical grade quality. Anhydrous sodium perchlorate was prepared by recrystallizing analytical grade  $\text{NaClO}_4 \cdot 2\text{H}_2\text{O}$  at  $90^\circ$  from an aqueous solution saturated at  $140^\circ$ . The crystals were filtered, dried at  $150^\circ$ , and stored in a vacuum desiccator. Tetrabutylammonium tetrafluoroborate was prepared by adding aqueous tetrafluoroboric acid to aqueous tetrabutylammonium hydroxide solution until the solution was neutral. Tetrabutylammonium tetrafluoroborate is almost insoluble in water but very soluble in acetonitrile and other organic solvents. It can be recrystallized from aqueous methanol.

Most reference compounds are either available commercially or easily prepared by standard methods. Of those not belonging to these categories, 2,2', 3,3', and 4,4'-dimethylbibenzyl were prepared according to the method given by Kunichika, Oka, and Sugiyama,<sup>25</sup> 2,4,5-trimethylbenzaldehyde according to the method given by Trahanovsky, Young, and Brown,<sup>26</sup> and 4-(2-methylbenzyl)-1,2-dimethylbenzene, 4-(3-methylbenzyl)-1,3-dimethylbenzene, and 3-(2,4,5-trimethylbenzyl)-1,2,4,5-tetramethylbenzene according to the method given by Baker, Banks, Lyon and Mann.<sup>27</sup>

*Electrolysis experiments.* The cell consisted of a jacketed vessel (volume about 60 ml), equipped with a cylindrical platinum anode (surface area about  $50 \text{ cm}^2$ ) and a platinum foil cathode. The reference electrode was the  $\text{Ag}/0.1 \text{ M AgClO}_4$  electrode. The anode potential was controlled by means of the Model 557 potentiostat from AMEL, Milan, Italy. The amount of charge passed through the electrolyte was measured by the Model 558 Integrator from the same company.

After adding to appropriate electrolyte to the cell, the electrolysis was run at a constant anode potential until 10 % of the calculated amount of charge (2 F/mole) had been passed. The cell temperature was kept at  $30^\circ$  by passing thermostated water through the jacket.

Then the acetonitrile was removed from the electrolyte at room temperature in a rotating evaporator and water added to the residue. The organic material was extracted into ether and the ether extracts analyzed by VPC (Perkin-Elmer 880 gas chromatograph, equipped with the Model D-24 Integrator) on a  $2 \text{ m} \times 0.3 \text{ cm}$  10 % SE-30 on Chromosorb W (80–100 mesh) column. In determining current yields, durene (for toluene and the xylenes), hexamethylbenzene (for durene), or 4-(2-methylbenzyl)-1,2-dimethylbenzene (for hexamethylbenzene) was used as an internal standard.

All products were identified by comparison with authentic specimen (retention time, mass spectrum).

\* Note added in proof. For further studies on this phenomenon, see Nyberg, K. *Chem. Commun.* 1969 774.

*Acknowledgements.* One of the authors (L.E.) gratefully acknowledges generous financial support from the *Swedish Natural Science Research Council* and *Carl Tryggers Stiftelse*.

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Received January 31, 1969.