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ON THE MECHANISM OF ANODIC ACETAMIDATION

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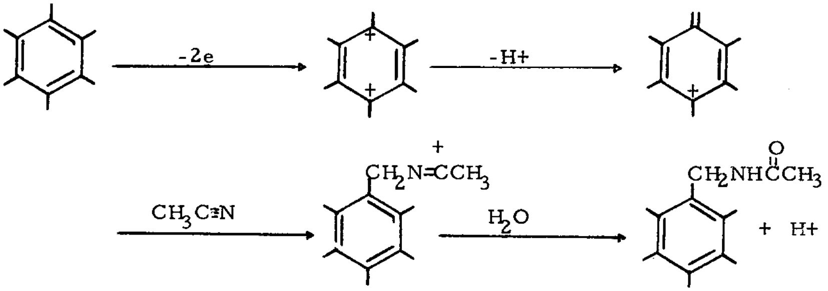
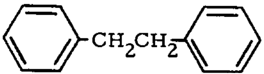
The recent communication by Eberson and Nyberg (1) has prompted us to report our results on the anodic acetamidation of toluene. They found that the electrolysis of hexamethylbenzene or durene in acetonitrile in the presence of sodium perchlorate produces N-benzylacetamides and propose the following mechanism to account for their results:



Experiments performed in our laboratory strongly indicate that this mechanism is not the only mechanism of anodic side chain substitution.

The electrolysis of toluene in wet acetonitrile in the presence of lithium perchlorate was found to produce products I-V. The structures of these compounds were confirmed by comparing their retention time in gas chromatography, infrared and mass spectra with those of authentic samples. Table I is a summary of several experiments in which either the supporting electrolyte or the water concentration in acetonitrile was varied.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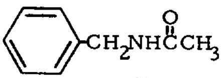
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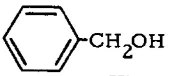
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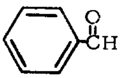
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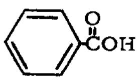

V

TABLE I

ANODIC ACETAMIDATION OF TOLUENE

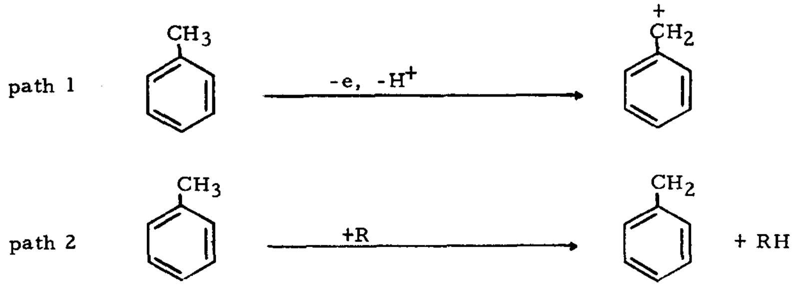
Experiment	Supporting Electrolyte	H_2O	Anode (1) Potential	Relative Distribution (2) of Volatile Products				
				I	II	III	IV	V
1	$LiNO_3$	5.5M	+2.7	30.9	37.0	3.7	16.1	12.3
2	$NaClO_4$	5.5M	+2.7	3.1	46.8	3.1	23.5	23.5
3	$LiClO_4$	5.5M	+2.7	3.3	43.1	9.9	18.3	25.4
4	$LiClO_4$	0.1M	+2.7	--	99.0	--	--	--
5	TEAP(3)	5.5M	+1.6	3.5	16.8	23.1	6.0	50.6
6	TEAP	5.5M	+1.8	27.0	23.8	31.1	13.6	4.5
7	TEAP	5.5M	+2.0	14.3	39.7	30.6	10.2	5.2
8	TEAP	5.5M	+2.4	13.5	26.9	25.0	13.5	21.1

(1) vs. saturated calomel electrode

(2) Percentages refer to percent of total volatile products as determined by gas chromatography

(3) Tetraethylammonium perchlorate

Of the five reaction products only bibenzyl (I) appears to have resulted from a one electron oxidation of toluene. The balance of the products may be explained by the formation of the benzyl carbonium ion which reacts with water or acetonitrile and water to form benzyl alcohol (III) or N-benzylacetamide (II). The other oxidation products (IV and V) may arise from the subsequent oxidation of benzyl alcohol. There are two conceivable ways in which the benzyl radical may arise. It could result from the direct electro-oxidation of toluene (path 1) or from hydrogen abstraction on toluene by other electro-generated free radicals (path 2).



Path 1 can be virtually eliminated by a consideration of the relative oxidation potentials of the benzyl radical and toluene. Toluene has an oxidative half-wave potential $E_{1/2(ox)}$ of + 2.3V (vs. S.C.E.) (2) while the benzyl radical would be expected to have an $E_{1/2\ (ox)}$ of less than + 1.2V (vs. S.C.E.) (3). Therefore, if the benzyl radical were formed at the anode, the potential of which being great enough to oxidize toluene, it would be immediately oxidized to the benzyl carbonium ion and no bibenzyl would be observed. If on the other hand, the benzyl radical is formed by a secondary process in the bulk of the solution, the coupling product would be expected since migration to the anode is necessary for further oxidation to occur. The formation of benzyl radicals by hydrogen abstraction on toluene by electrode generated nitrate radicals (4) and perchlorate radicals (5) has recently been reported.

The benzyl carbonium ion could conceivably form by a direct two electron oxidation of toluene or by anodic oxidation of the benzyl radical formed in path 2. We feel that the fact that this reaction takes place at anode potentials considerably below (+ 1.6V vs. S.C.E.) the $E_{1/2(ox)}$ of toluene (+ 2.3V vs. S.C.E.) is a strong argument against a direct 2-electron anodic oxidation as the predominant mode of this reaction. Eberson and Nyberg (1) reported the anodic acetamidation of both durene and hexamethylbenzene at anode potentials 0.7V lower than $E_{1/2(ox)}$ of the hydrocarbon and still operating at high currents (300-500 ma) (7). This would seem to imply that some process other than direct anodic oxidation of the substrate may be taking place. Another fact that suggests that the potentials employed by Eberson and Nyberg are not great enough for the direct anodic oxidation to be the predominant reaction is the fact that in the presence of as little as 3% water the major product was the corresponding alcohol (1). Lund has shown that anisyl alcohol can be oxidized at a few millivolts lower than anisole (8). The hydroxymethyl group would be expected to activate the aromatic nucleus toward anodic oxidation since electron donating groups exhibit this behavior (3). The fact that the benzyl alcohols obtained by Eberson and Nyberg are stable to the electrolysis condition is indicative that durene and hexamethylbenzene may be undergoing oxidation by a route such as path 1 rather than that suggested (1) by these authors.

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