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ELECTROCHEMICAL HYDROXYLATION OF NEGATIVELY SUBSTITUTED AROMATICS

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Many chemical procedures are known for introduction of hydroxy functions into aromatic compounds; however, few of these are generally applicable to both activated as well as deactivated aromatics. Substituted phenols have been prepared by electrochemical methods at the anode [1-3] as well as at the cathode [4-6], but again, these are not applicable to achieving negatively substiuted phenols. This note presents a new technique for preparation of aromatic phenols bearing negative substituents. Additionally, some insight is given into the electrochemical reactions of negatively substituted aromatics, a class of compounds whose direct oxidative electrochemistry has remained almost entirely unknown to date.

The discovery of this reaction evolved from studies with the medium, trifluoroacetic acid containing sodium trifluoroacetate as supporting electrolyte. We expected trapping of trifluoromethyl radicals, formed *via* Kolbe electrolysis, to occur with negatively substituted aromatics [7,8]; however, to our surprise only aryl trifluoroacetates were formed in addition to the gaseous Kolbe product (not isolated); *provided that electrolysis was performed at high positive potentials*. Among the aromatics studied were 1,4-dichlorobenzene, nitrobenzene and benzotrifluoride. Because of the very high $E_{1/2}$ values expected for these compounds and concomitant cooxidation of solvent, no meaningful oxidation potentials could be obtained in our solvent/supporting electrolyte solutions.

Electrolyses (Table I) were carried out using a PAR Model 173 potentiostat with a single or a 3-compartment cell[9] containing CF_3CO_2H/CF_3CO_2Na solution and 2-10% trifluoroacetic anhydride to ensure anhydrous conditions. The solution in the anode compartment was magnetically stirred under a N_2 atmosphere. The cathode was carbon or Pt. After electrolysis, the anolyte was poured into water, extracted with $HCCl_3$, the $HCCl_3$ extracts dried over a anhydrous $MgSO_4$, evaporated and the residue examined by GC on a 12' column of 20% SE-30 on Anachrome ABS. Table II compares the results of electrochemical acyloxylation of benzotrifluoride in different acid media under otherwise similar conditions. It is apparent that the acyloxylates may be obtained or the corresponding phenols by hydrolysis.

Taken together several pieces of evidence seem to substantiate a mechanism in which the aromatic substrate is electrooxidized directly, followed by nucleophilic attack of the cationic species by acyloxylate anion:

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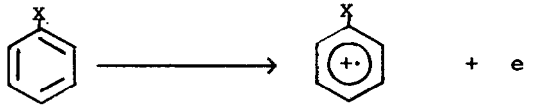
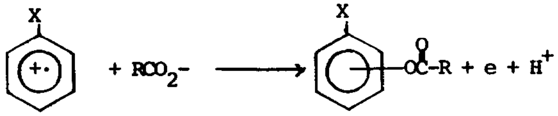


(1)



(2)

This evidence is as follows:

(i) The lowest current efficiency is observed for the aromatic expected to be most difficult to oxidize, i.e., nitrobenzene (Table II).

(ii) High positive electrolysis potentials are required.

(iii) The products are formed with a high <u>ortho</u> and <u>para</u> content, compared to <u>meta</u>. In a radical mechanism, i.e., <u>via</u> attack of $RCO_2.$ (from discharge of the anion) a high percentage of <u>meta</u> would be expected. Note that early work by Eberson and others[3] dismisses such a species.

(iv) The current efficiency of acyloxylation increases with increasing acid strength (Table II).

A competing anodic reaction of aromatic oxidation is discharge of the acyloxylate anion,

$$RCO_2^- \longrightarrow RCO_2. + e \qquad (3)$$

$$RCO_2. \longrightarrow R. + CO_2 \qquad (4)$$

$$2R. \longrightarrow R-R \qquad (5)$$

in which the sequence (3) to (5) is the well known Kolbe reaction.

Little or no $E_{1/2}^{oxid}$ data exists for carboxylates. However, it can be inferred on the basis of the results of Table II that the oxidation potential of carboxylates increases in positive value as the R-group becomes more electron withdrawing, resulting in a corresponding increase in the effective "window" or useful positive potential range of that medium.

The nucleophilic reactions of highly negatively substituted cation-radicals have not been previously studied. Our results apparently indicate that cation-radicals are formed and that the nucleophilic reactions of aromatic negatively substituted cation radicals are very similar to aromatics previously studied.[3]

Such questions as the role of adsorption of substrate, and the scope and limitations of this new electroorganic reaction with regard to other negatively substituted aromatics is under investigation.

TABLE I: ELECTROCHEMICAL TRIFLUOROACETOXYLATION OF NEGATIVELY SUBSTITUTED AROMATICS

Aromatic (conc.)	Solvent^a/ Supporting Electrolyte (conc.)	Anode Material (V vs SCE)	Temp. $^\circ$C.	Products^b (Current Efficiency,%) Isomer Distribution
1,4-Dichlorobenzene (2M)	TFA/NaTFA (1M), TFAA (10%)	Pt(3.4)^c	40° ^{d}	Trifluoroacetates (1.2); 2,5-dichlorophenol (43)
Nitrobenzene (0.5M)	TFA/NaTFA (0.5M), TFAA (2%)	Pt(4.3)^c	25°	Nitrophenols (29), o:m:p=2.6:4.3:1.1
Benzotrifluoride (0.2M)	TFA/NaTFA (0.5M) TFAA (5%)	C (3 to 5)^e	25°	Trifluoroacetates (56%), o/p=0.30; phenols (3.7%)
Benzotrifluoride (0.2M)	TFA/NaTFA (1.0M), TFAA (5%)	Pt (3 to 5)^e	25°	Trifluoroacetates (57%), o/p=0.39; phenols (9.7)

a) TFA, trifluoroacetic acid, reagent grade; NaTFA, sodium trifluoroacetate; TFAA, trifluoroacetic anhydride

b) Total of esters and phenols (Kolbe products not included).

c) Three-compartment cell was used to avoid possible reduction of substrate.

d) A higher than normal temperature was used to increase the substrate solubility.

e) One-compartment cell used, but the reference (SCE) was separated from the anode by a Luggin probe.

TABLE II: CURRENT EFFICIENCY OF ACYLOXYLATION OF BENZOTRIFLUORIDE AT Pt WITH ACID USED

Carboxylic Acid^a	pk_a (H_2O)	Total Current Efficiency of Products^b
CF_3CO_2H	(0)	67
$ClCH_2CO_2H^c$	2.9	10
HCO_2H	3.8	4.3
CH_3CO_2H	4.8	1.4

a) The electrolysis media contained the corresponding sodium salt (1M)

b) Total of esters and phenols (Kolbe products not included)

c) Electrolysis conducted at 55°C.

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