Short Communications

Studies on Electrolytic Substitution Reactions. X.[1] Anodic Trifluoroacetoxylation of Benzene and Deactivated Benzenes

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Anodic acetoxylation of aromatic compounds is limited to those substrates which are easier to oxidize than the acetic acid/sodium acetate medium.[2] Benzene derivatives containing electron-donating substituents are generally efficiently oxidized. Benzene itself is oxidized to phenyl acetate in low yield,[3] and deactivated benzene derivatives, such as benzotrifluoride or methyl benzoate, are not oxidized at all in acetic acid/sodium acetate.[4]

In trifluoroacetic acid it should be possible to oxidize even the latter compounds, since it has been shown that aliphatic hydrocarbons are oxidized in this medium,[5] which is more resistant toward oxidation than is acetic acid. It has also been reported that the cation radical intermediates in the oxidation of aromatic compounds, are more stable in trifluoroacetic acid than in less acidic media.[6-8]

We now give a preliminary report of the results from controlled potential oxidation of benzene and deactivated benzene derivatives in trifluoroacetic acid/1.0 M sodium trifluoroacetate. The reactions were carried out in a divided cell at a platinum anode until 10 % of the charge calculated for a two-electron process had been passed. This procedure was used in order to avoid further oxidation of the products.[4] Aryl trifluoroacetates were formed in all experiments and were converted into the

$$ArH \xrightarrow[\substack{CF_3COOH \\ CF_3COONa}]{Pt} ArOCOCF_3$$

$$\xrightarrow{H_2O} ArOH \qquad (1)$$

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Table 1. Anodic trifluoroacetoxylation of aromatic compounds. Product yield and isomer distribution (observed[a] and calculated).

| X in PhX | Isomer distribution | | | | | | Current yield (%) |
| | Observed | | | Calculated | | | |
	o	m	p	o	m	p	
H							27
COOCH$_3$	51	34	15	54	16	30	65
NO$_2$	22	59	19	30	43	27	60
CF$_3$	35	47	18	50	35	15	31
COCH$_3$	54	32	14	52	17	31	67
COPh	70	18	12	54	15	31	21
CN	45	30	25	42	30	28	10

[a] The products were analyzed as the corresponding phenols.

corresponding phenols before analysis because of their sensitivity towards moisture (eqn. 1). The results are shown in Table. 1. Current-potential curves for the solvent-supporting electrolyte system showed a steep current rise at 2.3 V vs. the Ag/Ag+ reference electrode. All the substrates shown in Table 1 were oxidized at potentials well below 2.3 V. An attempt to oxidize 1,4-dicyanobenzene was unsuccessful. In this experiment no change in the current-potential curve for the solvent-supporting electrolyte system was noticed upon addition of the substrate. On the other hand, dimethyl terephthalate was converted into its hydroxy derivative in a 60 % current yield.

The isomer distribution shown in Table 1 is of interest from a mechanistic point of view. It is now generally accepted that aromatic cation radicals are the primary species in the oxidation of aromatic compounds.[2,9,10] It has been suggested that the positive charge density in a ring position of an aromatic cation radical should determine the relative amount of nucleophilic attack at that position.[11-15] In the anodic acetoxylation of monosubstituted benzenes carrying an electron-donating substituent the ortho and para products predominate over the meta isomer, corresponding to the isomer distribution obtained in electrophilic aromatic substitution.[4] If an analogous mechanism prevails for benzene derivatives carrying an electron-withdrawing substituent one would expect the compounds shown in Table 1 to yield the meta
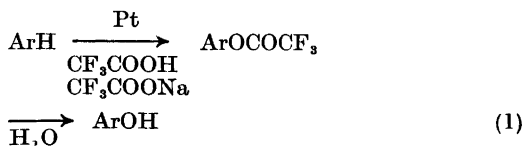
isomer predominantly on anodic substitution. The results in Table 1 do not, however, agree with this prediction. Instead they correlate reasonably well with the isomer distribution calculated from the positive charge distribution in the cation radicals, as calculated by the INDO method.[16-18] The results are shown in Table 1 and add further support to the suggestion that the site of attack by a nucleophile is determined by the positive charge density in a particular position of the cation radical.

From a preparative point of view the reaction is promising, since it allows the ready introduction of a hydroxy group into deactivated aromatic molecules. It is also noteworthy that some oxidations produce a large proportion of the *ortho* substituted phenol and are of possibly unique preparative value in this respect. Further work of mechanistic and preparative nature will be reported later. In a recent paper Miller *et al.* report the anodic oxidation of acetophene and ethyl benzoate in trifluoroacetic acid/methylene chloride using Et_4NBF_4 as the supporting electrolyte.[19] They obtained *ortho* substituted products in yields comparable to ours, but no *meta* substituted products.

Experimental. The electrolysis cell consisted of a 20 ml water-jacketed flat-bottomed glass cylinder with a four-neck flat flange lid equipped with a platinum foil anode, a platinum wire cathode, an $Ag/0.1$ M $AgOCOCF_3/CF_3COOH$ reference electrode, a drying tube and a magnetic stirrer bar. The separation of the anode compartment and the cathode was achieved by a ceramic cylinder. The oxidative potential was controlled with an Amel Model 557 Potentiostat.

Electrolysis was carried out in a 1 M NaOCOCF$_3$ solution in CF_3COOH (10 ml). The aromatic substrate (0.02 mol) and neutral alumina [20] (0.5 g) were added to the anode compartment and the electrolysis was run until 0.004 F had passed. The reaction mixture was then poured into boiling water (50 ml) in order to hydrolyze the aryl trifluoroacetates formed. After cooling, the mixture was extracted with ether or methylene chloride. The organic phase was washed with water and dried. Analysis was carried out on a Perkin-Elmer Model 880 Gas Chromatograph in connection with a Model D 26 Integrator utilizing a 2 m × 0.3 cm 5 % NPGS on Chromosorb W column. Identification of the products was based on comparison with authentic samples or by the use of mass spectrometry. Yields were calculated by integration of the GLC peaks after calibration by means of authentic samples.

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