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Indirect hydroxylation of aromatic rings using electrochemical methods

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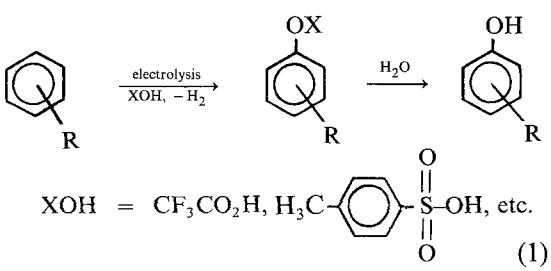
Hydroxylation of activated aromatic rings has been achieved by anodic substitution followed by hydrolysis. The nucleophiles employed are anions of trifluoroacetic acid and *p*-toluenesulphonic acid, which result in ring-deactivation upon monosubstitution and are easily hydrolysed. High yields at high substrate conversion for the electrochemical step were obtained in dry acetonitrile solutions by constant potential electrolysis at graphite or platinum anodes. Hydrogen evolution at a platinum cathode occurred in the same compartment. Preliminary experiments have shown that the electrolysis proceeds similarly in the presence of a second immiscible solvent (CCl_4 or di-n-butyl ether).

1. Introduction

Many important speciality chemicals contain, or are derived from, a hydroxyl group on an aromatic ring, e.g. the parabens (preservatives), 2,4-dichlorophenoxyacetic acid (herbicide) and *N*-acetyl-*p*-aminophenol (pain reliever) [1]. In general, aromatic hydroxylation is a difficult task and current methods suffer from nonspecificity, unwanted byproducts and severe reaction conditions. We have developed a fairly general method for the hydroxylation of aromatic rings by anodic substitution with oxygen nucleophiles followed by hydrolysis (Equation 1). The nucleophiles are anions of strong acids, such that the



(1)

product of the first anodic substitution is less susceptible to oxidation than the starting marterial. Thus, the electrolyses can be carried out to a high degree of conversion, in contrast to those which utilize anions of weaker acids [2, 3].

Hydroxylation of negatively substituted aromatics has been achieved through anodic substitution with acetate nucleophiles containing electron-withdrawing substituents and the corresponding acid as solvent (e.g. CF_3CO_2H/CF_3CO_2Na) [3–8]. However, this method is unsuccessful for aromatics with electron donating substituents (the aromatic apparently competes with the anion as nucleophile in this poorly-ionizing solvent [9], see below), and the high cost and low conductivity ($4 \times 10^{-4} \Omega^{-1} cm^{-1}$ for 1 M CF_3CO_2Na in CF_3CO_2H) of these solutions thwart commercial development of this technology. By using a polar solvent, CH_3CN, in which sodium trifluoroacetate has unusually high solubility (0.8 g ml^{-1}) we have been able to generate fairly conductive solutions (3×10^{-3} $\Omega^{-1} cm^{-1}$ for 1 M CF_3CO_2Na in CH_3CN) and perform anodic substitutions on positively-substituted aromatic rings with good yields and current efficiencies. We have extended this method to use the less expensive anion, *p*-toluenesulphonate.

2. Experimental details

All materials were reagent grade and used as received unless otherwise indicated. Tetraethylammonium *p*-toluenesulphonate (Aldrich) was

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0021–891X/86 $03.00 + .12

dried at 50° C for 12 h, transferred to a dry box under helium (Vacuum Atmospheres,Inc.), ground, triturated with dry diethyl ether and dried under vacuum. *p*-Toluene sulphonic acid monohydrate was recrystallized from chloroform and dried under vacuum at 60° C to yield the anhydrous form. Dry acetonitrile and n-butyl ether were prepared by distillation from CaH_2 and stored in the dry box. Carbon tetrachloride was distilled from anhydrous $MgSO_4$ and stored likewise.

Product identification and yields were determined by comparison to appropriate standards using gas chromatography (GC) (Perkin Elmer Model 900) and/or gas chromatography/mass spectroscopy (GC/MS) (Hewlett–Packard 5992A GC/MS System). The method of Bourne *et al.* [10] was used to prepare 1-naphthyl trifluoroacetate, 2-naphthyl trifluoroacetate, 2-phenylphenyl trifluoroacetate, 4-phenylphenyl trifluoroacetate and 4,4′-di-(trifluoroacetoxy)-biphenyl from the corresponding phenols.

2.1. *Preparation of p-(t-butyl)phenyl acetate [11]*

A mixture of *p*-(t-butyl)phenol (45 g), acetic anhydride (100 ml), and sodium acetate (10 g) was heated at reflux for 3 h followed by distillation of the acetic anhydride (25° C/5 mm) and then distillation at 90° C/1.5 mm to yield pure (by GC) *p*-(t-butyl)phenyl acetate.

2.2. *Preparation of p-acetoxytoluene [12]*

The procedure was analogous to the above. The product was distilled at 70° C/5 mm.

2.3. *Preparation of methyl p-methoxybenzoate [13]*

A mixture of methyl *p*-hydroxybenzoate (15.2 g, 0.1 mol), acetone (100 ml), CH_3I (9.3 ml) and K_2CO_3 (21 g) was heated at reflux for 5 h. The solids were removed by filtration and the solvent was removed by rotary evaporation to yield the pure white solid, methyl *p*-methoxybenzoate, which was dried under vacuum.

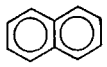
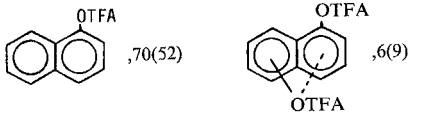
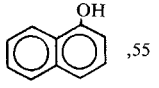
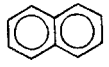
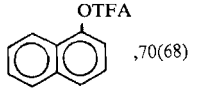
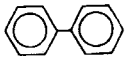
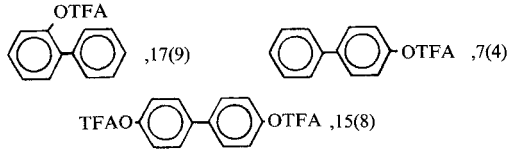
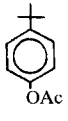
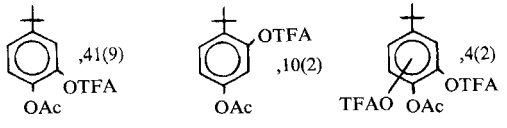
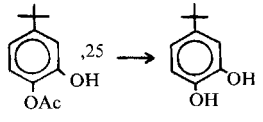
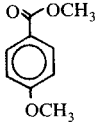
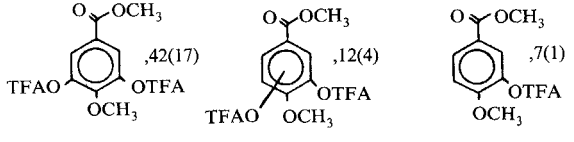
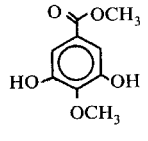
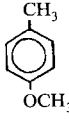
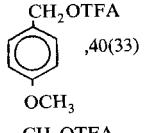
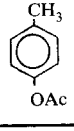
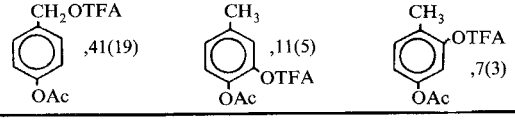
2.4. *Preparation of 1-naphthyl p-toluenesulphonate [14]*

A solution containing 1-naphthol (3.0 g), *p*-toluenesulphonyl chloride (7.6 g) in 50 ml of pyridine was stirred for 14 h. The resulting mixture was poured into 400 ml of ice-water and stirred for 15 min. This mixture was made basic with 50% $NaOH_{(aq)}$ and extracted with 3 × 50 ml of CH_2Cl_2. The combined CH_2Cl_2 extracts were dried (K_2CO_3), filtered, and the solvent was removed by rotary evaporation. The residue was recrystallized from hexane–chloroform to yield crystalline 1-naphthyl *p*-toluenesulphonate.

2.5. *General electrochemical procedures*

Constant potential electrolyses were performed using a Bioanalytical Systems, Inc. (BAS) SP2 Synthetic Potentiostat operated at the potentials listed in Table 1. The cell consisted of a 15-ml glass vial containing a magnetic stirrer, a graphite rod anode (working area $\sim 1\ cm^2$), a platinum gauze cathode (separated from the anode by ~ 1 mm), and a $AgCl_{(aq)}/Ag^0$ reference electrode (BAS). The electrolysis solutions consisted of 0.05 M substrate and 1 M CF_3CO_2Na in 8 ml of CH_3CN plus 2 ml of trifluoroacetic anhydride (TFAA). The TFAA was used as a water scavenger and in so doing was converted to trifluoroacetic acid (TFA, $pK_a = 0.2$) which provided the protons which were reduced at the cathode. Electrolyses with the *p*-toluenesulphonate anion in place of trifluoroacetate were performed as described above, except that all materials were carefully dried prior to use, and the electrolyses were performed in a dry box under helium. The solutions contained 0.05 M naphthalene, 0.2 M *p*-toluenesulphonic acid and 1 M tetraethylammonium *p*-toluenesulphonate in acetonitrile, and electrolyses were performed at 1.47 V versus $AgCl_{(aq)}/Ag^0$. At initial current densities of 50–100 mA cm^{-2} the voltage between anode and cathode was 3–5 V. The currents were plotted on a Houston 2111-6-5 High Speed X-Y Recorder (with time base) and the amount of charge passed was determined by manual integration. Product yields were determined by quantitative dilution and comparison, by GC, with appropriate standards. Hydrolysis of the

Table 1. Results of anodic substitution with sodium trifluoroacetate in acetonitrile

Substrate	*Applied potential**	*% Conversion*	*Electrolysis products, yields† (Current efficiency)*	*Hydrolysis products, overall yields*
	1.50	94		 ,55
	1.34	34		–
	1.70	~100		–
	1.85	97		
	1.85	100		
	1.37	~100		–
	1.74	93		–

* Versus $AgCl_{(aq)}/Ag^0$.
† Based on consumed starting material.
‡ OTFA = O_2CCF_3.

Table 2. GC/MS data for synthesized compounds, m/z (relative intensity)

Compound	*GC/MS data*
1-(Trifluoroacetoxy)naphthalene	240(M^+, 17), 143 ($M-CF_3CO_2$, 47), 115(100), 69(CF_3, 18)
Di-(trifluoroacetoxy)naphthalene	352(M^+, 2), 255($M-CF_3CO_2$, 4), 199(15), 133(29), 102(23), 76(16), 75(10), 69(CF_3, 100), 50(10)
2-(Trifluoroacetoxy)biphenyl	266(M^+, 22), 197($M-CF_3$, 100), 169($M-CF_3CO$, 57), 168(27), 153($M-CF_3CO_2$, 30), 141(66), 139(34), 115(65), 69(CF_3, 25)
4-(Trifluoroacetoxy)biphenyl	266(M^+, 14), 169($M-CF_3CO$, 90), 141(100), 115(84), 69(CF_3, 41)
4,4′-Di-(trifluoroacetoxy)biphenyl	378(M^+, 8), 139(18), 128(38), 127(15), 102(13), 69(CF_3, 100)
4-(t-Butyl)phenyl acetate	192(M^+, 6), 150($M-CH_2O$, 25), 136($M-C_4H_8$, 13), 135($M-C_4H_9$, 100), 107(16), 91(13), 77(8), 43(CH_3CO, 19), 41(10)
2-(Trifluoroacetoxy)-4-(t-butyl)phenyl acetate	304(M^+, 8), 262($M-CH_2CO$, 35), 248($M-C_4H_8$, 14), 247($M-C_4H_9$, 100), 229(35), 105(10), 91(10), 77(13), 69(CF_3, 12), 43(CH_3CO, 21)
3-(Trifluoroacetoxy)-4-(t-butyl)phenyl acetate	304(M^+, 8), 262($M-CH_2CO$, 37), 248($M-C_4H_8$, 13), 247($M-C_4H_9$, 100), 229(39), 77(15), 69(CF_3, 16), 43(CH_3CO, 57)
Di-(trifluoroacetoxy)-4-(t-butyl)phenyl acetate	416(M^+, 1), 359($M-C_4H_9$, 4), 304($M-CF_3CO_2$ + 1, 5), 262($M-CH_2CO-CF_3CO_2$ + 1, 30), 247($M-CF_3CO_2-C_4H_8$), 229(43), 135(10), 103(11), 77(14), 69(CF_3, 33), 43(CH_3CO, 53)
2-Acetoxy-5-(t-butyl)phenol	208(M^+, 2), 166($M-CH_2CO$, 21), 152($M-C_4H_8$, 10), 151($M-C_4H_9$, 100), 123(14), 43($M-CH_3CO$, 17)
4-(t-Butyl)catechol	166(M^+, 26), 151(M–O + 1, 100), 123(40), 105(17), 77(14), 41(14).
Methyl 4-methoxybenzoate	166(M^+, 32), 136($M-CH_2O$, 10), 135($M-CH_3O$, 100), 107(14), 92(12), 77(19)
Methyl 4-methoxy-3-(trifluoroacetoxy)benzoate	278(M^+, 46), 248($M-CH_2O$, 13), 247($M-CH_3O$, 100), 125(11), 122(15), 121(14), 119(10), 107(10), 79(25), 69(CF_3, 30), 59(14), 51(16)
Methyl 4-methoxy-3,5-di-(trifluoroacetoxy)benzoate	390(M^+, 32), 359($M-CH_3O$, 39), 262(23), 165(100), 137(20), 109(15), 69(CF_3, 50), 59(20), 53(19)
Methyl 4-methoxy-di-(trifluoroacetoxy)benzoate	390(M^+, 6), 360($M-CH_2O$), 329(89), 301(32), 99(40), 69(CF_3, 100), 51(24)
Methyl 4-methoxy-3,5-dihydroxybenzoate	198(M^+, 30), 167($M-CH_3O$, 19), 166($M-O_2$, 100), 123(40), 69(18), 53(19)
4-Methoxybenzyl trifluoroacetate	234(M^+, 14), 121($M-CF_3CO_2$, 100), 78(12), 77(13), 69(CF_3, 13)
4.Methylphenyl acetate	150(M^+, 28), 108($M-CH_2CO$, 100), 107($M-CH_3CO$, 72), 78(28), 77(50), 69(50), 43(CH_3CO, 78)
4-Acctoxybenzyl trifluoroacetate	262(M^+, 6), 220($M-CH_2CO$, 40), 107($M-CH_2CO-CF_3CO_2$, 100), 106(20), 78(16), 77(21), 69(CF_3, 26), 43(CH_3CO, 51)
4-Methyl-1-(trifluoroacetoxy)phenyl acetate	262(M^+, 9), 220($M-CH_2CO$, 76), 123(79), 107(31), 106(31), 77(22), 69(CF_3, 66), 43(CH_3CO, 100)
4 Methyl-3-(trifluoroacetoxy)phenyl acetate	262(M^+, 6), 220($M-CH_2CO$, 69), 151(17), 123(100), 95(18), 77(16), 69(CF_3, 44), 66(24), 43(CH_3CO, 85), 39(17)
1-Naphthyl *p*-toluenesulphonate	300(M + 2, 8), 299(M + 1, 25), 298(M^+, 100), 155(26), 144(13), 143(99), 115(81), 91(29), 89(11), 65(13)
Binaphthyl	255(M + 1, 24), 254(M +, 35), 253(M − 1, 31) 252(M − 2, 29), 239(16), 127($C_{10}H_7$, 31), 126($C_{10}H_6$, 100), 125($C_{10}H_5$, 55), 120(17), 113(48), 112(24)

aromatic trifluoroacetoxy substituents was complete in several hours after addition of 1 ml of water to the final electrolysis solution, or in 5 min after making the electrolysis solution basic (pH = 10) with $NaOH_{(aq)}$.

In the electrolyses with *p*-toluenesulphonate, it was necessary to dilute the electrolysis mixture with water (50 ml), extract with CH_2Cl_2 (3 × 20 ml) and concentrate by rotary evaporation prior to quantitative yield determination of 1-naphthyl *p*-toluenesulphonate by GC. The two-phase electrolyses were run on a mixture of 0.5 mmol naphthalene, 10 mmol of tetraethylammonium *p*-toluenesulphonate, 4 ml of CH_3CN, 0.3 g of anhydrous *p*-toluenesulphonic acid and 6 ml of the second solvent (CCl_4 or n-butyl ether). A separate layer of ~4 ml formed with both of these second solvents. Work-up of these electrolyses mixtures (to determine yield of 1-naphthyl *p*-toluenesulphonate) was performed as described above.

2.6. *Hydrolysis of 1-naphthyl p-toluenesulphonate*

A mixture of 1-naphthyl *p*-toluenesulphonate (0.15 g), NaOH (2 g), H_2O (4 ml) and dioxane (9 ml) was heated at reflux for 4 h in the dark. This two-phase solution was added to 50 ml of water, cooled in an ice bath and acidified with concentrated $HCl_{(aq)}$. The product was extracted with 3 × 20 ml of CH_2Cl_2 and this solution was dried ($MgSO_4$) and concentrated by rotary evaporation to yield 0.05 g (90%, by GC) of 1-naphthol.

2.7. *GC/MS data for synthesized compounds*

The GC/MS data for synthesized compounds, used for product identification are given in Table 2.

3. Results and Discussion

Equation 1 shows the general scheme for the indirect hydroxylation of aromatic rings. Typically, the initial electrolysis current density was 50–100 mA cm^{-2}, and at this current the voltage between anode and cathode was 3–5 V. The aromatic substrates, applied potentials, conversion percentages and product and current yields are listed in Table 1. Although these yields were obtained with a graphite anode, those obtained at a platinum anode with naphthalene, biphenyl and *p*-methylanisole substrates were equally good. In contrast, the other substrates required potentials in excess of 2 V to achieve significant substrate conversion at a platinum electrode, and poor yields were obtained. Hydrolysis of the trifluoroacetoxy derivatives was complete in 5 min in aqueous base (pH = 10) at ambient temperatures.

The best results were obtained with naphthalene as the substrate. Surprisingly, identical yields (70%) were obtained at 35% and 95% conversion although higher current efficiencies and a purer product (Table 1) were obtained at lower conversion. In no case was 2-trifluoroacetoxy-naphthalene observed. At higher conversion a small yield (6%) of a di-(trifluoroacetoxy)-naphthalene was observed, but no di-hydroxy products were detected after hydrolysis and work-up. The overall isolated yield of pure (by GC) 1-naphthol after mild basic hydrolysis was 55%. Although biphenyl was used up at a high current efficiency, a multitude of mono-, di- and tri-trifluoroacetoxy products were observed. Of these, 2-(trifluoroacetoxy)biphenyl, 4-(trifluoroacetoxy)biphenyl and 4,4′-di-(trifluoroacetoxy)-biphenyl were identified in 17, 7 and 15% yields, respectively, after passage of 2 F mol^{-1} of charge. Apparently, biphenyl is much less selective in the position at which it stabilizes the intermediate positive charge prior to attack by the nucleophile [2–9].

Electrolysis of 4-t-butylphenyl acetate required a higher potential (1.85 V) for a fast rate of conversion (95% in 1 h). The principal products were 4-t-butyl-2-(trifluoroacetoxy)phenyl acetate (41% yield) and 4-t-butyl-3(trifluoroacetoxy)-phenyl acetate (10% yield), along with a small amount (4% yield) of a di-TFA product. Mild hydrolysis (by addition of water to the electrolysis solution) gave 2-hydroxy-4-t-butylphenyl acetate with an overall yield of 25%. Hydrolysis in aqueous base yielded the commercially important 4-t-butylcatechol (yield undertermined). As indicated in Table 1, low current efficiencies were obtained at the high potential required for this electrolysis, and some corrosion of the graphite

anode was observed. This problem was minimized by electrolysing at 1.75 V (~20 mA initial current) which increased the current efficiencies in Table 1 by a factor of 3. Substrates which are less effective at stabilizing the transient radical cation (and thus are oxidized at a higher potential) would be difficult to hydroxylate by this route.

The introduction of two trifluoroacetoxy groups onto methyl 4-methoxybenzoate for ultimate synthesis of gallic acid (after hydrolysis) was investigated. This di-substitution successfully yielded 42% methyl-4-methoxy-2,6-di-(trifluoroacetoxy)benzoate along with a 12% yield of another di-substituted product. The high potential (1.85 V) required for this conversion resulted in low current efficiencies and, again, some electrode corrosion.

Side-chain substitution was achieved for substrates containing a strong electron-donating substituent para to a methyl group on an aromatic ring, and thus provides a route to certain benzylic alcohols. Side-chain acetoxylation has been reported, but the yields and degree of substrate conversion were generally low [2, 15–20]. Accordingly, electrolysis of *p*-methoxytoluene at 1.34 V yielded 40% *p*-methoxybenzyl trifluoroacetate and reasonable current efficiency (33%) at 100% conversion. Although the amount of ring substitution with this substrate was very small (< 2%), ring substitution amounted to approximately 30% of the mono-TFA products from *p*-acetoxytoluene (Table 1). The acetate substitutent is a weaker electron donor and is less effective at stabilizing the positive charge on the aromatic carbon in the para position, which ultimately leads to benzylic substitution [9]. As expected, a higher potential was required for oxidation of this substrate (Table 1). The products were 4-acetoxybenzyl trifluoroacetate, 4-acetoxy-3-(trifluoroacetoxy)toluene, and 4-acetoxy-2-(trifluoroacetoxy)toluene in yields of 41, 11 and 7%, respectively. A small yield (5%) of a di-TFA product was also observed. Hydrolysis of these side-chain TFA products was not attempted.

The above method using sodium trifluoroacetate and trifluoroacetic anhydride in acetonitrile was quite successful, but commercial utilization is unlikely except for very high value-added hydroxylations due to the expensive nature of these TFA materials (although recycle of the trifluoroacetic acid should be feasible). Thus, a less expensive nucleophile and the elimination of the anhydride drying agent were sought. An inexpensive source of an anion that will provide an electron-withdrawing group upon anodic substitution, is *p*-toluenesulphonic acid ($pK_a = -1.3$). In a manner similar to the trifluoroacetoxy group, this should minimize further oxidation of the mono-substituted product. Indeed, electrolysis of a dry CH_3CN solution containing 0.05 M naphthalene, 0.2 M *p*-toluenesulphonic acid and 1 M tetraethylammonium *p*-toluenesulphonate at 1.47 V versus $AgCl_{(aq)}/Ag^0$ yielded 80% 1-naphthyl *p*-toluenesulphonate after 93% conversion (64% current efficiency). Basic hydrolysis of 1-naphthyl *p*-toluenesulphonate in refluxing dioxane–water yielded 90% 1-naphthol. Hence, the overall yield of 1-naphthol from naphthalene by this pathway was 72%.

In a similar electrolysis performed with a 2 : 1 ratio of nucleophile to substrate, a lower, yet acceptable, yield of 1-naphthyl *p*-toluenesulphonate was produced (49% at 48% conversion of naphthalene). The current efficiency for production of this product was only 31%. A substantial amount (8% yield) of binaphthyl was obtained under these conditions. Apparently, a large excess of the anionic nucleophile (*p*-toluenesulphonate in this case) is necessary to prevent competition of the weakly nucleophilic naphthalene ring. When this latter electrolysis was carried out to a higher degree of conversion (91%), a slightly lower yield (45% with a current efficiency of 19%) of 1-naphthyl *p*-toluenesulphonate was obtained along with a 1% yield of binaphthyl.

For ultimate scale-up and implementation of a flow cell operting at constant current, a second solvent, which dissolves the product but is immiscible with the above electrolysis solution, was sought for use in continuous extraction of the product. Of the *dry* solvents investigated, 1,2-dichloroethane, methylene chloride, dioxane, tetrahydrofuran, toluene and benzene dissolved the product but were fully miscible with the electrolysis solution. Hexane and cyclohexane were immiscible, but did not dissolve 1-naphthyl *p*-toluenesulphonate. Ethyl ether, n-butyl ether and carbon tetrachloride met the above criteria,

but diethyl ether was deemed too volatile for use in a continuous flow system.

Constant potential electrolyses of two-phase solutions were successful with CCl_4 and n-butyl ether, but in both cases some of the extraction solvent invaded the electrolysis layer (see Experimental section). The electrolysis with CCl_4 converted naphthalene at a high current efficiency and 1-naphthyl *p*-toluenesulphonate was the major product (yield undetermined). It was necessary to perform this electrolysis in a two-compartment cell or with a large excess of acid to prevent the reduction of CCl_4 and subsequent production of 1-chloronaphthalene [21, 22]. With n-butyl ether a 73% yield of 1-naphthyl *p*-toluenesulphonate (44% current efficiency) was obtained after conversion of 93% of the naphthalene. This electrolysis was run at a 20 : 1 ratio of *p*-toluenesulphonate to naphthalene. Reducing this ratio to 2 : 1 resulted in substantial coupling of naphthalene. (Binaphthyl comprised 35% of the product.)

Although these preliminary results are encouraging, they have not yet been extended to a flow cell operating at constant current.

4. Conclusions

A general method has been presented for the hydroxylation of aromatic hydrocarbons which are oxidized in acetonitrile at potentials less than or equal to 1.85 V versus $AgCl_{(aq)}/Ag^0$. The procedure appears to require an electron-donating substituent or polyaromatic ring. Appropriate substituents or polyaromatic rings are also necessary to direct the position of the intermediate radical cation and yield highly selective hydroxylation. Particularly impressive are the high yields at high conversion of substrate which is often difficult to achieve with electro-organic syntheses [23]. Success here is most likely due to the electron-withdrawing ability of the trifluoroacetoxy and *p*-toluenesulphonyl substituents, which renders the aromatic ring of the product more difficult to oxidize than the starting material.

Corrosion of the graphite anode, which was observed at 1.85 V, limited the usable anodic potential, at least for the TFA electrolyses. Higher potentials (up to 2.5 V) were attainable with a platinum anode, but product yields were poor for the electrolyses of substrates requiring potentials in excess of 2 V. Other electrode materials (such as other forms of carbon, PbO_2, RuO_2/Ti and IrO_2/Ti) were not investigated.

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