Electrochemical Acylation of Aromatic Compounds

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Summary Acylation of a range of aromatic compounds has been effected by the *in situ* generation of an energetic acylating species during the anodic oxidation at vitreous carbon of 2,3,5,6-tetramethoxyquinol diacetate in trifluoroacetic acid solution.

Anodic deacylation of durohydroquinone diacetate to give the corresponding quinone has been described[1] and on the basis of cyclic voltammetry an ECE mechanism was suggested which involved the rapid expulsion of two acylium ions. The relevant anodic peak potential was at

$+1{\cdot}90$ V (*vs.* S.C.E.) which precludes oxidation in the presence of the generally more easily oxidised aromatic compounds which might be expected to trap the acylium ion.

We report here on the anodic oxidation of 2,3,5,6-tetramethoxyquinol diacetate, a reaction which can be used for the generation of acylium ions at a relatively low potential.

Cyclic voltammetric experiments show that at vitreous carbon oxidation at $+1{\cdot}05$ V (*vs.* Ag wire) gives the corresponding quinone. An additional oxidation peak at $+1{\cdot}25$ V (*vs.* Ag wire) was shown, by cyclic voltammetry on the tetramethoxyquinone, to relate to further oxidation of the quinone. For these experiments *ca.* 1·4 mM-solutions were used in 4:1 CH_2Cl_2–CF_3CO_2H using Bu_4NClO_4 (0·25 M) supporting electrolyte.

TABLE

Aromatic compound[a]	Coulombic yield of acyl derivatives (%)[b]
Benzene	24·5
Toluene	90·8[c]
p-Xylene	78·2
Mesitylene	90·5
Durene[d]	low[e]
Naphthalene[b]	low[e,g]
Anisole	34·4[c,e]

[a] 1:1 Mixture with CF_3CO_2H–0·5 M-Bu_4NClO_4 except where stated to contrary. [b] Based on g.l.c. analysis using internal standards and calculated for 2F mol^{-1}. [c] *para*-Acylation only. [d] Durene (5g), CF_3CO_2H (10 ml); CH_2Cl_2 (10 ml), 0·5 M-Bu_4NClO_4. [e] Competing oxidation of hydrocarbon. [f] Naphthalene (5 g), CF_3CO_2H (30 ml), CH_2Cl_2 (10 ml), 0·5 M-Bu_4NClO_4. [g] $\alpha:\beta$ Ratio = 1:2.

Preparative-scale electrolyses (Table) on 0·1—2·0 g of quinol acetate in 7—15 ml of solvent were carried out at $+1{\cdot}05$ V (*vs.* Ag wire) using a conventional divided cell with vitreous carbon rod anode and a platinum cathode. The acidic medium (CF_3CO_2H–0·5 M-Bu_4NClO_4) ensured that added aromatic substrates were the most nucleophilic species present. In most cases *ca.* 70% of the theoretical amount of electricity was passed. Nuclear acylation was observed which confirms Parker's hypothesis[1] and which is capable of development into a useful preparative reaction. Qualitative experiments have shown that graphite anodes can also be used with success. Relative to the duration of the electrolyses (*ca.* 4 h) 2,3,5,6-tetramethoxyquinol diacetate decomposes slowly in the acidic medium (CF_3CO_2H–Bu_4NClO_4). The very reactive mesitylene is acylated by the mixture to some extent but the amount of non-electrochemical acylation taking place during the electrolyses is small. Preliminary experiments using acetonitrile solution show that mesitylene can also be acylated electrochemically without added trifluoroacetic acid. Benzene is not acylated in the absence of current.

The acyl derivatives were isolated by distillation and the quinone by filtration. The recovered quinone is easily reconverted into the quinol diacetate (Zn dust–Ac_2O). Cathodic reduction of quinones to quinol diacetates (Hg cathode, MeCN–Ac_2O) is an alternative route.[2]

The acylium ion produced anodically according to the above method is more reactive than the acylating species active in acetic acid–trifluoroacetic anhydride[3] which do not, for instance, acylate benzene or toluene. Anodic acylation gives, for naphthalene, the α- and β-isomers in the ratio 1:2, (*cf.* 1:9 using[4] AcCl–$AlCl_3$ in $PhNO_2$), which also indicates a small, reactive, acylating species.

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[4] P. H. Gore in 'Friedel-Crafts and Related Reactions,' ed. G. A. Olah, Interscience, New York, 1964, vol. 3, part 1, p. 242.