

Electrochemical Reduction of Fluorinated Aromatic Carboxylic Acids

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Pentafluorobenzoic acid has been selectively electrochemically reduced in good yield to 2,3,5,6-tetrafluorobenzoic acid, 2,3,5,6-tetrafluorobenzyl alcohol, and pentafluorobenzyl alcohol. Electrochemical reduction of 4-chloro-, 4-amino-, 4-methoxy-, and 4-hydro-tetrafluorobenzoic acids, pentafluorobenzaldehyde, ethylpentafluorobenzoate, and pentafluorobenzamide has been studied. The mechanism of the reduction process, and therefore the products obtained, is governed by the potential of the cathode, the acidity, and the type of ions present in the base electrolyte.

THE electrochemical reduction of hydrocarbon aromatic carboxylic acids and their derivatives is well known^{1,2} and the polarographic reduction of pentafluorobenzoic acid has been studied.³ Pentafluorobenzaldehyde⁴ and perfluoroaliphatic carboxylic acids⁵ have been reduced to fluorinated alcohols and aldehydes in moderate yields, with lithium aluminium hydride. Recently, the electrochemical reduction of trifluoroacetic acid⁶ has been reported. In a preliminary publication⁷ we briefly reported the electrochemical reduction of pentafluorobenzoic acid in aqueous sulphuric acid. Here we amplify

that report and also describe the reduction of pentafluorobenzoic acid and its derivatives in other media.

Table 1 shows the results of the reduction of pentafluorobenzoic acid on mercury in aqueous sulphuric acid at different cathodic potentials. At -1.10 V *vs.* s.c.e. no organic reaction occurred. When the cathode potential was more negative (-1.20 V *vs.* s.c.e.) the principal reaction involved replacement of the *para*-fluorine atoms in the molecule yielding, 2,3,5,6-tetrafluorobenzoic acid as the major product. As the cathode potential was increased still further the reaction became less selective with respect to fluoride-ion displacement

¹ S. Swann, jun., 'Technique of Organic Chemistry,' Interscience, London, 1956, vol. II, p. 385.

² F. Fichter, 'Organische Electrochemie,' Steinkopff, Dresden, 1942, p. 253.

³ W. W. Bartle and B. R. Eggins, *J. Polarog. Soc.*, 1966, **12**, 89.

⁴ B.P. 985,650.

⁵ U.S.P. 2,568 500/1951.

⁶ R. Woods, *Electrochim. Acta*, 1970, **15**, 815.

⁷ P. Carrahar and F. G. Drakesmith, *Chem. Comm.*, 1968, 1562.

and reduction of the carboxy-group occurred to an increasing extent, such that at -1.50 V the products were pentafluorobenzyl alcohol and 2,3,5,6-tetrafluorobenzyl alcohol, the major product being the one in which the *para*-fluorine atom was not replaced.

Current efficiencies of the organic reactions in sulphuric acid solutions were *ca.* 50% in the initial stages of a reaction but as the concentration of organic com-

using this base electrolyte and controlled potentials, highly specific reactions could be achieved to produce compounds which contained a *para*-hydrogen atom in good chemical and coulomb yields. It has been shown that hydrogen^{8,9} in a fluoroaromatic system can act as a functional group, *e.g.* transmetallation with butyllithium can take place to give a fluoro-organic lithium compound and application of this technique could allow

TABLE 1
Reduction of pentafluorobenzoic acid in aqueous sulphuric acid

Potential (V) w.e. vs. s.c.e.	Temp. (°C)	C ₆ F ₅ ·CO ₂ H recovered %	C ₆ HF ₄ ·CO ₂ H % yield ^b	C ₆ F ₅ ·CH ₂ ·OH % yield ^b	C ₆ HF ₄ ·CH ₂ ·OH % yield ^b
-1.10	21	100	0	0	0
-1.20	20	10	73	6	20
-1.30 ^a	25	0	0	24	48
-1.40 ^a	30	0	0	35	40
-1.50 ^a	30	0	0	45	33

^a Approximately same number of coulombs passed. ^b Based on C₆F₅·CO₂H reacted.

pound became depleted then hydrogen evolution was the principal electrochemical process resulting in overall current efficiencies for total conversion of acid to alcohols of <20%. Thus it had been shown that the reduction of pentafluorobenzoic acid could be achieved electrochemically and, to a limited extent, selectivity of reaction obtained by adjustment of the cathode potential. The next objectives were to improve the coulomb efficiency of the organic process and to increase the specificity of the reaction, *i.e.* to stop the process at a predetermined point along the reaction path.

the synthesis of many derivatives of highly fluorinated benzyl alcohols produced electrochemically in this way.

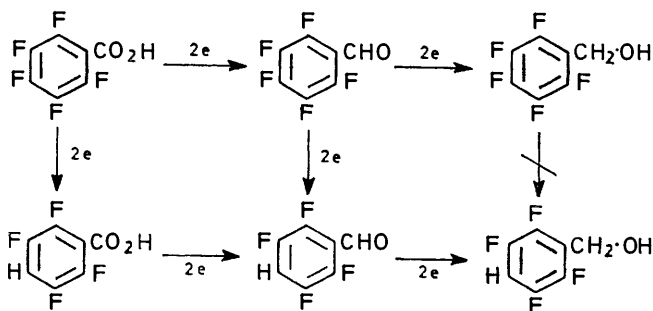
Results of preceding experiments showed that the products of reduction were dependent not only on

TABLE 2
Reduction of pentafluorobenzoic acid in aqueous
(0.2M)Et₄NBF₄ solution

	Potential (V)		C ₆ HF ₄ ·CO ₂ H % yield	C ₆ HF ₄ ·CH ₂ ·OH % yield
	w.e. vs. s.c.e.	Temp. (°C)		
At mercury surface	-1.60	25	25	30
	-2.00	25	40	55
	-2.40	25	20	40
At lead sur- face	-1.50	25	90	0
	-1.60	25	90	5
	-1.75	25	48	40
	-2.40	25	10	75

cathode potential but also on the nature of the base electrolytes. It appeared that in order to produce pentafluorobenzyl alcohol, that is, the reduction product in which no fluorine had been replaced it was essential to carry out the reaction in a more acid medium. In order to test this hypothesis, a number of reactions were performed in perchloric acid solutions of different concentrations and therefore different values for the Hammett acidity function.

As the results show (Table 3), for concentrations greater than 30% the main product was pentafluorobenzyl alcohol together with a trace of compound in which the *para*-fluorine had been replaced. The specificity of these reactions appeared to be independent of cathode potential. It is interesting to note that no 2,3,5,6-tetrafluorobenzoic acid is produced at -1.20 V in perchloric acid unlike the situation in sulphuric acid solution. Experiments in which dilute solutions of perchloric acid were used were not specific in their production of pentafluorobenzyl alcohol but produced approximately equal mixtures of pentafluoro- and tetrafluorobenzyl alcohol. The relationship between Hammett



When the reduction of pentafluorobenzoic acid was performed in aqueous tetraethylammonium tetrafluoroborate (Table 2) only products which contained the *p*-hydro-function were obtained. At a mercury pool cathode, the products over a range of potentials were mixtures of 2,3,5,6-tetrafluorobenzoic acid and 2,3,5,6-tetrafluorobenzyl alcohol. At more negative potentials relatively more alcohol was produced. When a lead cathode was held at a potential of -1.50 V (s.c.e.) the sole product was 2,3,5,6-tetrafluorobenzoic acid. As the potential was increased to -2.40 V (s.c.e.) reaction of the carboxy-group occurred and the principal product was 2,3,5,6-tetrafluorobenzyl alcohol.

Current efficiencies of electrochemical reductions of fluoroaromatic carboxylic acids in tetra-alkylammonium tetrafluoroborate solutions were 70–80%. Thus, by

⁸ R. J. Harper, E. J. Soloski, and C. Tamborski, *J. Org. Chem.*, 1964, **29**, 2385.

⁹ R. D. Chambers, F. G. Drakesmith, and W. K. R. Musgrave, *J. Chem. Soc.*, 1965, 5045.

acidity of the base electrolyte and the products obtained was also borne out by reactions carried out in other weakly acidic base electrolytes (Table 4) such as acetic acid and standard buffer solutions in which, although conversions were very low, the product was solely 2,3,5,6-tetrafluorobenzyl alcohol. In none of these reactions was an aldehydic product isolated. This was presumably because no stable, non-reducible *gem*-diol is formed by pentafluorobenzaldehyde¹⁰ and because the

benzoic acid at the same potential which showed that the principal reaction was one of fluorine replacement and that reduction of the carboxy-group did not occur to any great extent. The results of reactions involving other *para*-substituents were consistent with those observed from reactions of the parent pentafluorobenzoic acid in that the general rule obtained that reactions performed in acid solution tended to favour retention of the original *para*-substituent, whereas reaction in alkylammonium

TABLE 3

Reduction of pentafluorobenzoic acid in aqueous perchloric acid

Potential (V) w.e. vs. s.c.e.	% Perchloric acid	Temp. (°C)	C ₆ F ₅ ·CO ₂ H recovered %	C ₆ F ₅ ·CH ₂ ·OH % yield	C ₆ HF ₄ ·CH ₂ ·OH % yield
-1.20	35	5	100	0	0
-1.30	35	5	10	70	<1
-1.60	35	10	0	60	<1
-2.00	7	10	0	40	38
-2.00	30	10	0	60	<1
-2.00	50	10	0	70	<1

TABLE 4

Potential (V) w.e. vs. s.c.e.	Base electrolyte	pH	Temp. (°C)	C ₆ F ₅ ·CO ₂ H recovered %	C ₆ F ₅ ·CH ₂ ·OH % yield	C ₆ HF ₄ ·CH ₂ ·OH % yield
-2.90	HOAc/NaOAc	3.4	20	>95	0	1
-3.50	HOAc/NaOAc	3.4	20	>95	0	2
-1.40	HOAc	2.1	20	100	0	0
-2.00	Buffer solution	4	20	90	0	5

reduction potential of the aldehyde group was less cathodic than the reduction potential of the carboxy-group, so that when reduction of the carboxylic acid function did occur, any aldehyde produced immediately reacted to give an alcohol. The likelihood of this cascade process was confirmed (Table 5) when it was shown that pentafluorobenzaldehyde was readily reduced in sulphuric acid at -1.20 V to give pentafluoro- and tetrafluoro-benzyl alcohol together with a small amount of intractible polymeric material.

At more negative potentials (-1.30 V) the reaction proceeded more rapidly and produced principally pentafluorobenzyl alcohol, demonstrating the greater susceptibility of the aldehyde group to reduction. Table 6 shows the results of reduction reactions of pentafluorobenzamide and ethyl pentafluorobenzoate. Whereas attempts to reduce ethyl pentafluorobenzoate were not successful, pentafluorobenzamide was smoothly reduced to pentafluorobenzyl alcohol as the principal product, and 2,3,5,6-tetrafluorobenzyl alcohol. This lack of reactivity of the ester compared with the amide is probably due to the greater basicity of the amide nitrogen over the oxygen of the ester which allows easier protonation of the amide. This is borne out by the much greater solubility of pentafluorobenzamide than ethyl pentafluorobenzoate in aqueous sulphuric acid.

In the study of the reactions of *para*-substituted derivatives of pentafluorobenzoic acid (Table 7) the observation that 2,3,5,6-tetrafluorobenzoic acid was not reduced at -1.20 V in aqueous sulphuric acid compared well with the results obtained from the reduction of pentafluoro-

salt solution tended to favour elimination of this substituent with replacement by hydrogen.

A more detailed study of the results also reveals information on the susceptibility of the individual *para*-substituent towards elimination. Thus it was observed

TABLE 5

Reduction of pentafluorobenzaldehyde

Potential (V)	Base electrolyte	C ₆ F ₅ ·CH ₂ ·OH % yield	C ₆ HF ₄ ·CH ₂ ·OH % yield
w.e. vs. s.c.e.			
-1.20	20% H ₂ SO ₄	50	10
-1.30	20% H ₂ SO ₄	80	12
-2.50	0.2M- [Et ₄ N] ⁺ [BF ₄ ⁻] sol	20	63

TABLE 6

Reduction of pentafluorobenzamide and ethyl pentafluorobenzoate in aqueous sulphuric acid

Potential (V)	Temp. (°C)	C ₆ F ₅ ·CH ₂ ·OH % yield	C ₆ HF ₄ ·CH ₂ ·OH % yield
w.e. vs. s.c.e.			
Amide			
-1.10	25	<1	<1
-1.20	25	58	20
-1.40	25	75	16
-1.60	30-40	70	18
Ester			
-1.40	25	<1	<1
-2.00	25	<1	<1
-2.30	25	<1	<1

that the substituents were in increasing order of susceptibility to replacement, NH₂ > F ≈ Cl > OMe.

With the exception of the amino-group, whose reactions are probably complicated by zwitterion formation, this order is similar to that observed for ease with

¹⁰ P. E. Iverson and H. Lund, *Acta Chem. Scand.*, 1967, **21**, 389.

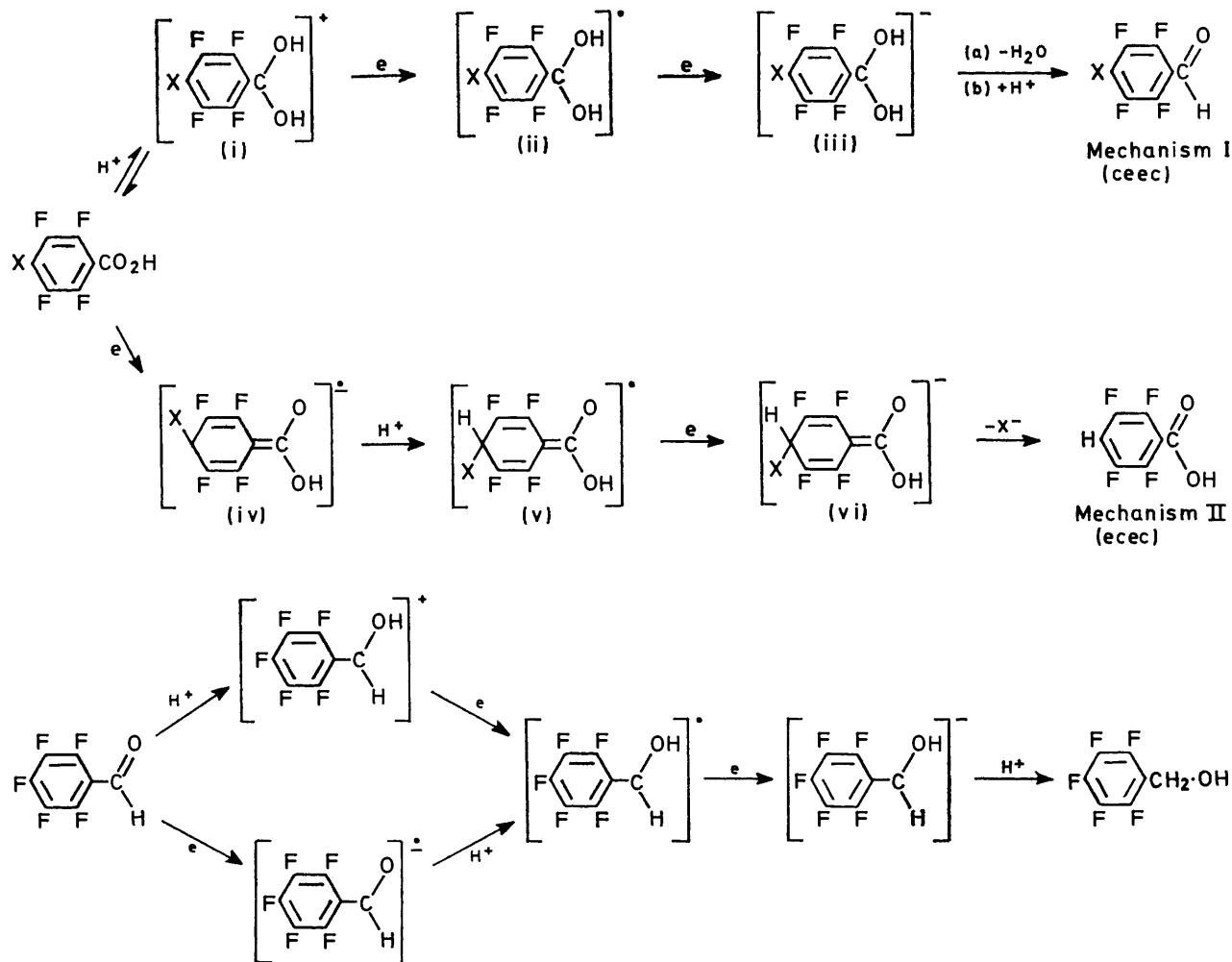
TABLE 7
Reduction of *para*-substituted fluorobenzoic acids

Starting material	Base electrolyte	Potential (V) w.e. vs. s.c.e.	HC ₆ F ₄ ·CO ₂ H	Products	HC ₆ F ₄ ·CH ₂ ·OH
XC ₆ F ₄ ·CO ₂ H X = Cl	35% HClO ₄	-1.80	0	30%	50%
	20% H ₂ SO ₄	-1.30	17%	16%	35%
X = F	0.2M-[Et ₄ N] ⁺ [BF ₄ ⁻]	-2.00	20%	0	35%
	35% HClO ₄	-1.60	0	60%	1%
X = OCH ₃	20% H ₂ SO ₄	-1.50	0	45%	33%
	0.2M-[Et ₄ N] ⁺ [BF ₄ ⁻]	-2.40	10%	0	75%
X = NH ₂	20% H ₂ SO ₄	-1.40	0	80%	0
	0.2M-[Et ₄ N] ⁺ [BF ₄ ⁻]	-2.00	0	40%	40%
X = H	35% HClO ₄	-1.50	0	0	60%
	0.2M-[Et ₄ N] ⁺ [BF ₄ ⁻]	-2.20	0	0	80%
	20% H ₂ SO ₄	-1.20	0	0	0

which the groups are displaced from carbon atoms in nucleophilic substitution reactions. Although this type of aromatic addition-elimination reaction¹¹ is a complicated matter also depending on the nucleophilic power of the attacking reagent and on the polar and steric effects of substituents it is interesting to observe this correlation between the elimination of groups from an S_N2 transition state and the proposed electrochemically generated anion described below. Although no attempt

was made to determine in detail the kinetic and mechanistic steps involved in these reactions it is possible from the experimental results to suggest some likely steps that may occur under the various reaction conditions employed. The main problem is to explain why in strong acid reaction of the carboxy-function is preferred and in tetraethylammonium tetrafluoroborate solution replacement of the *para*-substituent occurs so readily.

Possible mechanistic explanations are shown below:



¹¹ J. Miller, 'Aromatic Nucleophilic Substitution,' Elsevier, London, 1968, p. 9.

Two different reactions, mechanism I and mechanism II, operate and when poor selectivity is observed, *e.g.* in 20% sulphuric acid solution, these reactions take place simultaneously.

Mechanism I is that most likely to occur in strongly acidic electrolytes where the carboxylic acid exists principally in its protonated form (i). Two-electron transfer to this produces firstly, radical (ii) and then, anion (iii). Elimination of water from this labile gem-diol followed by protonation, produces pentafluorobenzaldehyde which then goes on to react in a similar fashion.

Mechanism II is possibly that which obtains in the presence of quaternary ammonium ions and weakly acidic electrolytes, where the carboxylic acid is not protonated by the medium. Electron transfer to the unprotonated acid produces radical anion (iv), which then adds a proton to give radical (v). Further electron transfer yields anion (vi) which then readily eliminates anion X^- to revert to the aromatic structure of *p*-hydro-tetrafluorobenzoic acid. Elimination of fluoride ion by electrochemically generated species from highly fluorinated unsaturated cyclic molecules to give aromatic compounds is well known.¹² *p*-Hydro-tetrafluorobenzoic acid could then be reduced to *p*-hydro-tetrafluorobenzyl alcohol *via* *p*-hydro-tetrafluorobenzaldehyde providing the potential was sufficiently cathodic.

The experimental results would suggest that mechanism II operates at less negative potentials in a given medium than does mechanism I. Also, the presence of quaternary ammonium salts appears to have a catalytic effect on the reduction compared with reactions in solutions of similar pH not containing tetra-alkylammonium ions (see Tables 2 and 4). This catalytic activity probably results from the adsorption of tetra-alkylammonium salts at the cathode¹³ causing a change in the fall of potential from the electrode surface into the solution, facilitating electron transfer through their environment. Alternatively, the quaternary ammonium ions could form an ion pair with the incipient radical anion which would reduce the energy of the transition state and reduce the activation energy of the next electron-transfer step.

Another possibility is that of participation of electrochemically generated hydrogen atoms in these reactions, especially in quaternary ammonium salt solutions, where it is known that these salts catalyse the reaction $H_3O^+ \xrightarrow{e} H \cdot + H_2O$, compared with other salt solutions of the same pH.

EXPERIMENTAL

Compounds used as base electrolytes, sulphuric acid, perchloric acid, and tetraethylammonium tetrafluoroborate were of AnalaR Reagent grade where possible. Tetraethylammonium tetrafluoroborate was also prepared by reaction of tetraethylammonium bromide with sodium

tetrafluoroborate and recrystallisation of the precipitated salt from aqueous methanol.

Pentafluorobenzoic acid and most of its derivatives used were commercial samples from Imperial Smelting Corporation Limited and Fluorochem Limited. *p*-Methoxytetrafluorobenzoic acid was synthesised by nucleophilic displacement of fluoride ion by sodium ethoxide from pentafluorobenzoic acid in methanol solution.

Ethyl pentafluorobenzoate was prepared by esterification of pentafluorobenzoic acid with ethanol in the presence of concentrated sulphuric acid, and pentafluorobenzamide by ammonolysis of ethylpentafluorobenzoate with anhydrous ammonia in diethyl ether.

Vapour-phase Chromatography.—A Perkin-Elmer model F11 chromatograph fitted with a hot-wire detector system was used for analytical scale v.p.c. Peak areas were determined directly using a digital print out integrator (Kent Chromolog) coupled to the amplifier output. The columns used were carbowax 20M/TPA on Chromosorb W. and diisodecyl phthalate on Chromosorb W.

Free carboxylic acids are normally difficult to examine using v.p.c. and because of this a new technique was developed. It was found that by using an injection port temperature in excess of 300 °C it was possible to flash decarboxylate the acids to give the aromatic moiety and carbon dioxide, *e.g.* pentafluorobenzoic acid gave pentafluorobenzene and carbon dioxide, *p*-methoxytetrafluorobenzoic acid gave *p*-hydro-tetrafluoroanisole and carbon dioxide. Shortly after this technique was devised here Tamborski¹⁴ reported a similar method in the open literature. A Wilks Model 41 i.r. micro-cell v.p.c. attachment was used to record the spectra of eluted compounds. For preparative-scale v.p.c. a Perkin-Elmer model F21 was used with columns of the same stationary phase as the analytical instrument.

I.r. spectra were run on a Unicam SP 200 spectrometer. Mass spectra were obtained from an A.E.I. MS12 instrument. N.m.r. spectra were obtained from Varian A-60 and Perkin-Elmer R.10 spectrometers with $CFCl_3$ and Me_4Si as internal references. Elemental analyses were carried out at the University of Durham.

Electrolysis.—The glass cells used for current voltage measurements and preparative work had a cathode compartment of 70-ml capacity, separated from the anode compartment by a coarse glass frit. The anode was a simple platinum flag (2 cm × 2 cm) in a solution of the base electrolyte. The ground-glass sockets in the cell head allowed the fitting of a mini-stirrer, thermometer well, nitrogen gas bubbler, and saturated calomel reference electrode. All potentials reported are relative to the saturated calomel electrode. Electrical contact to the mercury pool cathode (12.5 cm²) was made through a metal-glass seal.

The cathode potential was controlled by means of a potentiostat (Amel Model 555, or a custom-built model incorporating a DC 300 W amplifier). The total current passed during electrolysis was measured by means of an electronic integrator (Amel Model 558).

The usual procedure involved a potential sweep on the base electrolyte followed by a sweep on a solution of the organic compound in the base electrolyte. Analysis of the *I/V* curves obtained indicated potentials at which electrochemical reactions occurred. Suitable potentials were

¹² A. M. Doyle, A. E. Pedler, and J. C. Tatlow, *J. Chem. Soc. (C)*, 1968, 2740; A. M. Doyle and A. E. Pedler, *ibid.*, 1971, 282.

¹³ J. D. Littlehailes, *Chem. and Ind.*, 1970, 77.

¹⁴ R. J. de Pasquale and C. Tamborski, *Chem. and Ind.*, 1968, 771.

selected from these curves and preparative experiments carried out under potentiostatic conditions.

Reactions were normally carried out on 1-g to 5-g of starting material. At the end of an electrolysis the cell contents were extracted with an organic solvent and the products were analysed by the usual techniques.

Detailed experimental procedures are given for reactions typical of those whose results are reported in the Tables.

Reduction of Pentafluorobenzoic Acid in Perchloric Acid.—Pentafluorobenzoic acid (4 g) was dissolved in 35% perchloric acid solution (70 ml) and electrolysed in the cell described above with a mercury cathode held potentiostatically at -1.60 V (s.c.e.) at 10° .

The electrolysis was continued until five times the theoretical numbers of coulombs for the organic reduction had passed. The cell contents were extracted with methylene dichloride and the organic layer was separated, dried (Na_2SO_4), and the solvent removed by distillation to yield the product (2.3 g). Analytical and preparative scale v.p.c. showed this to be a mixture of 2,3,5,6-tetrafluorobenzyl alcohol (<1% yield) and pentafluorobenzyl alcohol (60% yield) m.p. 32° , i.r. spectrum identical with that of an authentic sample,* δ (CDCl_3) 5.2 (2H, t, J 1.6 Hz, CH_2) and 7.2 p.p.m. (1H, s, OH). ^{19}F N.m.r. spectroscopy showed three peaks highfield of CFCl_3 reference, at 166 (multiplet), 158 (multiplet) and 148 p.p.m. (multiplet) in the intensity ratio 2 : 1 : 2; m/e 198(P), 181, 177, 150, 117, and 105.

Reduction of Pentafluorobenzoic acid in Tetraethylammonium Tetrafluoroborate.—Pentafluorobenzoic acid (3 g) was dissolved in aqueous 0.2M-tetraethylammonium tetrafluoroborate solution (70 ml) and electrolysed in the cell described above with a mercury cathode held potentiostatically at -2.00 V (s.c.e.) at 25° . The reaction was continued until the initial current (300 mA) had fallen to 4.5 mA, when the electrolysis was stopped. The electrolyte was extracted with diethyl ether and the organic layer was separated and shaken with saturated sodium hydrogen carbonate solution. This alkaline aqueous layer was separated, neutralised, and extracted with diethyl ether and dried (Na_2SO_4). Removal of the ether by distillation gave 2,3,5,6-tetrafluorobenzoic acid (1.1 g, 40%) characterised by its S-benzylthiuronium derivative, m.p. 170° (lit.,¹⁵ m.p. 173°) (Found: C, 49.2; H, 2.7; F, 22.9. $\text{C}_{15}\text{H}_{12}\text{F}_4\text{N}_2\text{O}_2\text{S}$ requires C, 50.0; H, 3.3; F, 21.1%). The reaction product was also decarboxylated as described above to give carbon dioxide and a compound whose v.p.c. retention time and i.r. spectrum were identical to an authentic specimen of 2,3,5,6-tetrafluorobenzene; m/e 194(P), 177, 150, 149, 130, and 99.

The original organic layer from the hydrogen carbonate

extraction was dried (Na_2SO_4) and the solvent was removed by distillation to give 2,3,5,6-tetrafluorobenzyl alcohol (1.4 g, 55%), m.p. $32-34^\circ$ (Found: C, 46.7; H, 1.95; F, 41.5. $\text{C}_7\text{H}_4\text{F}_4\text{O}$ requires C, 46.7; H, 2.2; F, 42.0%), δ (CDCl_3) 3 (1H, m, aromatic H), 5.2 (2H, t, CH_2), and 5.8 p.p.m. (1H, s, OH). ^{19}F n.m.r. spectroscopy showed two peaks highfield of CFCl_3 reference, at 151 p.p.m. (multiplet) and 143 p.p.m. (multiplet), in the intensity ratio 1 : 1; m/e 180(P), 163, 159, 132, 99, 81.

Reduction of 2,3,5,6-Tetrafluoro-4-methoxybenzoic acid in Sulphuric Acid.—2,3,5,6-Tetrafluoro-4-methoxybenzoic acid (3 g) was dissolved in 20% sulphuric acid (70 ml) and electrolysed in the cell described above with a mercury cathode at -1.40 V (s.c.e.) at 10° . Electrolysis was continued until five times the theoretical number of coulombs for the organic reduction had passed; the cell contents were then extracted with methylene dichloride. The organic layer was separated, dried (Na_2SO_4), and the solvent removed by distillation to give 2,3,5,6-tetrafluoro-4-methoxybenzyl alcohol (2.25 g, 80%), m.p. $36-37^\circ$ (Found: C, 46.0; H, 2.6; F, 36.65. $\text{C}_8\text{H}_6\text{F}_4\text{O}_2$ requires C, 45.7; H, 2.85; F, 36.2%); m/e 210(P), 193, 189, and 119. The i.r. and n.m.r. spectra were consistent with this structure.

Reduction of 4-Chloro-2,3,5,6-tetrafluorobenzoic acid in Perchloric Acid.—4-Chloro-2,3,5,6-tetrafluorobenzoic acid (4 g) was dissolved in 35% perchloric acid (70 ml) and electrolysed in the cell described above with a mercury cathode at -1.80 V (s.c.e.) at 5° . Electrolysis was continued until five times the theoretical number of coulombs for the organic reaction had passed; the cell contents were then extracted with methylene dichloride. The organic layer was separated, dried (Na_2SO_4), and the solvent removed by distillation to give the products (7.7 g). Analytical and preparative scale v.p.c. showed this to be a mixture of 2,3,5,6-tetrafluorobenzyl alcohol (50%) and 4-chloro-2,3,5,6-tetrafluorobenzyl alcohol (30%), m.p. $60-61^\circ$ (Found: C, 39.2; H, 1.55; F, 35.7; Cl, 17.1. $\text{C}_7\text{H}_3\text{ClF}_4\text{O}$ requires C, 39.15; H, 1.4; F, 35.4; Cl, 16.6%). The i.r. n.m.r. and mass spectra were consistent with this structure.

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* Imperial Smelting Corp. Ltd.

¹⁵ D. J. Alsop, J. Burdon, and J. C. Tatlow, *J. Chem. Soc.*, 1962, 1801.