

Electro-organic Reactions. Part I. The Cathodic Cleavage in Methanol Solution of Benzylic Carbon–Oxygen and Carbon–Fluorine Bonds

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Controlled potential electroreduction of methanol solutions of *p*-methoxycarbonylbenzyl acetate and *p*-methoxycarbonylbenzyl methyl ether results in cleavage to methyl *p*-toluate in high yield and with good current efficiency. Substituted benzotrifluorides may similarly be cleaved to the substituted toluene. For efficient reduction an electron-accepting substituent (CO₂Me or CN) is required which must be *para* to the group undergoing cleavage. The effect of substituents and of added acetic acid on the product distribution, together with voltammetric data, indicate an e.c.e. mechanism. Attempts to effect partial defluorination of the CF₃ group, including the use of a rapidly rotating lead disc electrode, failed.

ELECTRON transfer to an organic molecule often results in the loss by cleavage of a substituent in those cases where the substituent can form a stable anion or radical. In particular the reductive cleavage of organic halides has been much studied.¹ Substituents which are viable anionic leaving groups and which are attached to benzyl or phenacyl residues have been shown to be cleaved relatively easily by cathodic reduction. Lund² reduced at a mercury cathode a series of phenacyl derivatives to acetophenone. Elving and Leone³ found that phenacyl fluoride was reduced smoothly to acetophenone at -1.35 V (*vs.* s.c.e.) and at an even lower potential [-0.9 V (*vs.* Ag–AgCl)] $\alpha\alpha\alpha$ -trifluoroacetophenone is converted into acetophenone.⁴ The trifluoromethyl group has also been found to be susceptible to reduction to a methyl group in aromatic compounds containing a

It has been reported that for nitrobenzyl halides in acetonitrile solution⁶ halide ion is lost from the anion radical and it seems that the rate of loss of halide is greatest when the nitro-group is *ortho* or *para* to the benzylic halogen. We have also reported,⁷ in preliminary form, on the range of products formed in the cathodic reduction of benzyl ethers, acetates, and substituted benzotrifluorides. We herein report fully the results of preparative scale electrolyses of compounds which bear in a benzylic position substituents which are good anionic leaving groups.

RESULTS AND DISCUSSION

Preparative Scale Reduction and Major Products.—Early experiments with *p*-methoxycarbonylbenzyl

TABLE I
Preparative scale reduction^a in methanol

Starting material	Cathode (V <i>vs.</i> s.c.e.)	Major product	Yield ^b (%)	Current ^c efficiency (%)
<i>p</i> -MeO ₂ CC ₆ H ₄ CH ₂ OMe	Pb (–1.85 to –2.00) ^d	<i>p</i> -MeO ₂ CC ₆ H ₄ CH ₃	71	50
<i>p</i> -MeO ₂ CC ₆ H ₄ CH ₂ OMe	Hg (–2.0 to –2.10) ^d	<i>p</i> -MeO ₂ CC ₆ H ₄ CH ₃	76	50
<i>p</i> -MeO ₂ CC ₆ H ₄ CH ₂ OMe	Pb (–1.9)	<i>p</i> -MeO ₂ CC ₆ H ₄ CH ₃	79	68
<i>p</i> -MeO ₂ CC ₆ H ₄ CH ₂ OMe	Hg (–1.9)	<i>p</i> -MeO ₂ CC ₆ H ₄ CH ₃	78	71
<i>p</i> -MeO ₂ CC ₆ H ₄ CH ₂ OMe	Hg (–1.9)	<i>p</i> -MeO ₂ CC ₆ H ₄ CH ₃	78	71
<i>p</i> -MeO ₂ CC ₆ H ₄ CH ₂ OAc	Pb (–1.8)	<i>p</i> -MeO ₂ CC ₆ H ₄ CH ₃	95	76
PhCOCH ₂ OAc	Pb (–1.8)	PhCOCH ₃	20	11
		PhCH(OH)CH ₃	54	56
<i>p</i> -MeO ₂ CC ₆ H ₄ CF ₃	Pb (–2.0)	<i>p</i> -MeO ₂ CC ₆ H ₄ CH ₃	60	52
<i>o</i> -MeO ₂ CC ₆ H ₄ CF ₃	Pb (–2.0)	<i>o</i> -MeO ₂ CC ₆ H ₄ CH ₃	42	34
		<i>o</i> -HOCH ₂ C ₆ H ₄ CF ₃	27	15
<i>m</i> -MeO ₂ CC ₆ H ₄ CF ₃	Pb (–2.0)	<i>m</i> -MeO ₂ CC ₆ H ₄ CH ₃	11	13
		<i>m</i> -HOCH ₂ C ₆ H ₄ CF ₃	ca. 5	ca. 5
<i>p</i> -NCC ₆ H ₄ CF ₃	Pb (–1.8)	<i>p</i> -NCC ₆ H ₄ CH ₃	58	54

^a Substrate 0.2M, tetra-*n*-butylammonium acetate (0.5M), controlled potential. ^b Based on amount of starting material consumed. ^c Calculated for 2, 4, or 6 faraday mol^{–1} as appropriate. ^d Constant current density (*ca.* 0.07 A cm^{–2}), sodium acetate (0.63M).

sulphonamide function *para* to the group being cleaved.⁵ An activating group is clearly necessary because benzotrifluoride itself is electrochemically inert at potentials more anodic than -2.0 V (*vs.* s.c.e.) (see footnote on p. 1905.⁵

¹ J. W. Sease, F. G. Burton, and S. L. Nichol, *J. Amer. Chem. Soc.*, 1968, **90**, 2595; J. Grimshaw and J. S. Ramsey, *J. Chem. Soc. (B)*, 1968, 60; S. Wawzonek, R. C. Duty, and J. H. Wagenknecht, *J. Electrochem. Soc.*, 1964, **111**, 74; O. R. Brown, H. R. Thirsk, and B. Thornton, *Electrochim. Acta*, 1971, **16**, 495.

² H. Lund, *Acta Chem. Scand.*, 1960, **14**, 1927.

³ P. J. Irving and J. T. Leone, *J. Amer. Chem. Soc.*, 1957, **79**, 1546.

methyl ether involved reduction at mercury at an uncontrolled potential and in the presence of sodium acetate.⁸ The results displayed in Table I confirm the early results but show that the reductive cleavage is more efficient if tetrabutylammonium acetate is used as the

⁴ J. H. Stocker and R. M. Jenevein, *Chem. Comm.*, 1968, 934.

⁵ H. Lund, *Acta Chem. Scand.*, 1959, **13**, 192.

⁶ J. G. Lawless, D. E. Bartak, and M. D. Hawley, *J. Amer. Chem. Soc.*, 1969, **91**, 7121.

⁷ J. P. Coleman, H. G. Gilde, J. H. P. Utley, and B. C. L. Weedon, *Chem. Comm.*, 1970, 738.

⁸ R. F. Garwood, Naser-ud-din, and B. C. L. Weedon, *Chem. Comm.*, 1968, 923.

supporting electrolyte. Lead has also proved to be a suitable cathode material for this work.

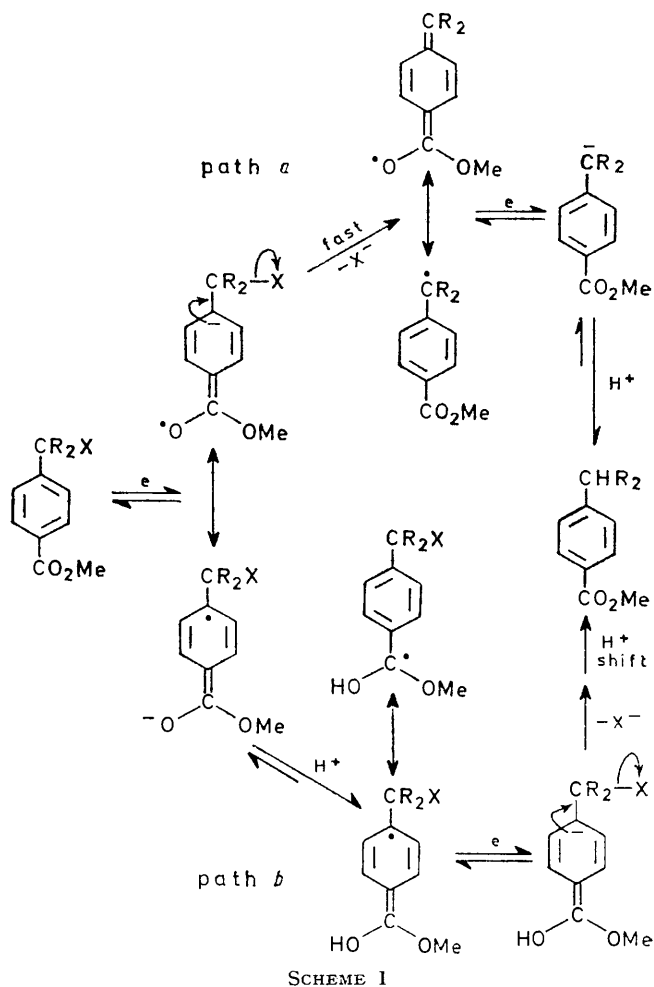
Controlled potential electrolysis in methanol solution, at a lead cathode, was accordingly carried out for a series of substrates bearing viable leaving groups in benzylic positions. The products resulting from such experiments are also summarised in Table I.

At cathode potentials controlled in the region of -1.8 V (*vs.* s.c.e.) the major product is indeed that of reductive cleavage. An exception is the case of phenacyl acetate in which the major process is reduction of the carbonyl group to give 1-phenylethanol. It was also found that exhaustive electrolysis of *p*-methoxycarbonylbenzyl acetate at a much more cathodic potential (-2.3 V) gave *p*-methylbenzyl alcohol as the major product, *i.e.* reductive cleavage and reduction of the ester group had taken place. Esters are not easily reduced at the cathode (see polarographic results, Table 4) and it is likely that in this case the reduction of the methoxycarbonyl substituent is subsequent to cleavage and not concurrent. Support for this view comes from the electrolysis of methyl *p*-toluate at -2.3 V which resulted in relatively inefficient (*ca.* 50%) production of a mixture of 4-methylbenzyl alcohol and 4-methylbenzaldehyde. It is not likely that the methoxycarbonyl group of *p*-methoxycarbonylbenzyl acetate is more easily reduced than that of methyl *p*-toluate [$E_1 -1.75$ V (*vs.* Ag-AgI) in dimethylformamide].

An activating, electron-accepting substituent such as methoxycarbonyl or cyano is required for efficient cleavage and it must be *ortho* or *para* to the group undergoing cleavage. The relative efficiencies of cleavage in the *ortho*-, *meta*-, and *para*-isomers of $\text{MeO}_2\text{CC}_6\text{H}_4\text{CF}_3$ demonstrate this point (Table 1). The *ortho*- and *para*-isomers are cleaved smoothly whereas electrolysis of a methanolic solution of the *meta*-isomer gave as a large part of the product (*ca.* 40%) a high boiling liquid (90–140° at 0.5 mmHg). According to t.l.c. analysis this high boiling fraction contained at least five compounds and the mass spectrogram of the mixture had peaks at *m/e* 380, 363, 331, 321 (<5%), 208 (100), 188 (30), 175 (80), and 173 (50). The molecular weight of the starting material is 204. In addition to this set of products, which though unidentified are clearly very different from those produced from other members of the series, the behaviour upon electrolysis was seen to be different. During reaction the cathode was sheathed in an intense yellow colour. This observation is consistent with the formation of a radical ion which is protonated slowly and from which fluoride ion expulsion is also relatively slow. The reactions producing the high molecular weight compounds are obviously complicated and further comment must await their identification.

The results of the preparative scale experiments described above are accommodated in the e.c.e. mechanisms summarised for the *para*-series in Scheme 1. Such mechanisms allow for the requirement of *ortho*- or *para*-electron-accepting substituents. If pathway *a* operates then reduction of the benzyl radical must be rapid; for

reduction of *p*-methoxycarbonylbenzyl methyl ether the corresponding bibenzyl was shown to be absent as an authentic sample could easily be detected (see Experimental section). Cyclic voltammetry shows that in dimethylformamide solution *m*- $\text{CF}_3\text{C}_6\text{H}_4\text{CO}_2\text{Me}$ is reduced reversibly in a one-electron process whereas the *para*-isomer is reduced irreversibly in a two-electron process.⁹ In methanol solution, in preparative scale reduction, the behaviour of the *meta*-isomer differs from that of the



para-isomer in the manner described above. These observations lend attraction to pathway *b* of Scheme 1 because it is generally accepted that protonation at oxygen is much faster than at carbon¹⁰ and the reduced charge at oxygen for the radical ion derived from *m*- $\text{CF}_3\text{C}_6\text{H}_4\text{CO}_2\text{Me}$ would account for slow protonation even in methanol.

That, on a preparative scale, there can be competition between protonation of the radical anion and loss of an anion is shown by the results of electrolysis in the presence of an efficient proton donor. A solution of *p*-methoxy-

⁹ J. H. P. Utley, unpublished results.

¹⁰ C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Cornell Univ. Press, Ithaca, 1953, p. 566.

carbonylbenzyl methyl ether in dry methanol was electrolysed at constant current density (0.15 A cm^{-2}) in the presence of anhydrous sodium acetate (0.5M) and acetic acid (0.5M) using a lead cathode (potential -1.5 to $-1.8 \text{ V vs. s.c.e.}$). The results of product analysis are given in Table 2.

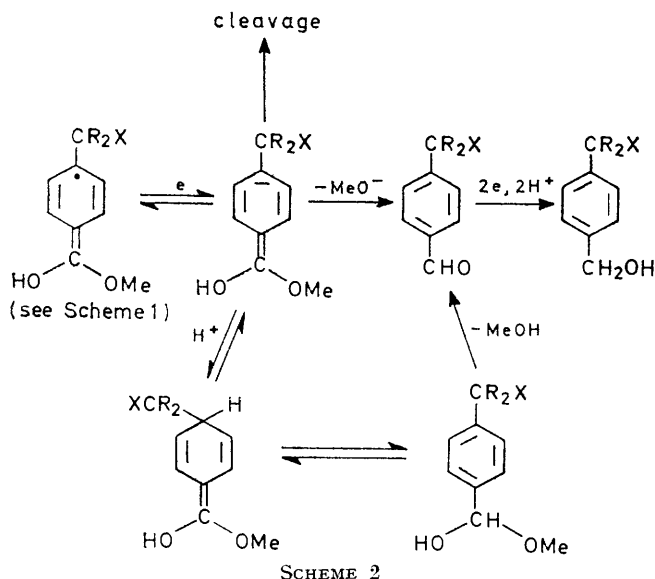
TABLE 2
Electrolysis of $p\text{-MeO}_2\text{CC}_6\text{H}_4\text{CH}_2\text{OMe}$ in the presence of acetic acid^a

Product	Relative yield (%)
Recovered starting material	11
$p\text{-MeC}_6\text{H}_4\text{CHO}$	13
$p\text{-MeC}_6\text{H}_4\text{CO}_2\text{Me}$	21
$p\text{-MeC}_6\text{H}_4\text{CH}_2\text{OH}$	17
$p\text{-MeOCH}_2\text{C}_6\text{H}_4\text{CHO}$	11
$p\text{-MeOCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{OH}$	27

^a Constant current density (0.15 A cm^{-2}), lead cathode [-1.5 to $-1.8 \text{ V (vs. s.c.e.)}$], methanol solution, sodium acetate (0.5M), acetic acid (0.5M).

Because of the similarity of the cathode potentials necessary for electrolysis with or without added acetic acid it is unlikely that the protonated substrate is the form undergoing electron transfer in the acidic solution. We suggest therefore that in the presence of acetic acid the protonation of the intermediate radical-ion competes favourably with cleavage (Scheme 2).

Attempted Partial Cleavage of the CF_3 Group.—Cathodic cleavage of fluorine from a trifluoromethyl group is



almost always complete. In the reduction of $\alpha\alpha\alpha$ -trifluoroacetophenone it proved possible to interrupt the reaction to produce the monofluoro-derivative.⁴ It did not prove possible however partially to reduce the trifluoromethyl group in our system. In one attempt methyl p -(trifluoromethyl)benzoate was reduced at a

* Stepwise cathodic defluorination of benzotrifluoride in dimethylformamide has recently been achieved and g.l.c. retention times are in the order $\text{PhCF}_3 < \text{PhCH}_3 < \text{PhCHF}_2 < \text{PhCH}_2\text{F}$ (H. Lund, personal communication).

rapidly rotating lead disc cathode in the hope of effecting enhanced diffusion into bulk solution of partially defluorinated intermediates. The conditions are summarised in Table 3.

TABLE 3
Electrolysis of $p\text{-MeO}_2\text{CC}_6\text{H}_4\text{CF}_3$ at a rotating lead disc cathode^a

Solvent	$\text{CH}_3\text{CN-MeOH (9:1)}$	CH_3CN	HCONMe_2
Current density (A cm^{-2})	0.25	0.25	0.125

^a Supporting electrolyte Bu_4NOAc (0.25M); rotation rate 3600 r.p.m. ; $2 \text{ faraday mol}^{-1}$ used.

In every case g.l.c. analysis of the volatile components of the product mixture showed no component with retention time intermediate between those of the starting material and methyl p -toluate and no component of longer retention time was detected.* Conclusions drawn from this result must be qualified however by the fact that in dimethylformamide at least the major product is one of two-electron reduction and relatively small amounts of methyl p -toluate are formed.⁹

The reduction of compounds containing two trifluoromethyl groups also results in the complete cleavage of fluorine from one or both of the groups. The compounds studied were methyl 2,4- and 2,6-bis(trifluoromethyl)benzoate and complicated product mixtures were obtained from both reductions. Exhaustive electrolysis of the 2,4-isomer [0.2M in methanol, Bu_4NOAc (0.6M), Pb cathode, $-1.7 \text{ V (vs. s.c.e.)}$] gave at least six products which were separated by g.l.c. The major component (*ca.* 35%) was, according to n.m.r. data and accurate mass measurement of the molecular ion, either methyl 2-methyl-4-(trifluoromethyl)benzoate or methyl 4-methyl-2-(trifluoromethyl)benzoate. The second most abundant product (*ca.* 23%) was the fully cleaved methyl 2,4-dimethylbenzoate.

Methyl 2,6-bis(trifluoromethyl)benzoate is less easily reduced, presumably because of steric inhibition of mesomerism involving the methoxycarbonyl group. However, similar electrolysis at $-2.0 \text{ V (vs. s.c.e.)}$ gave by g.l.c. analysis two major components (totalling *ca.* 65%) and six minor ones. Of the two major components that at longest retention time comprised two incompletely resolved products. The major product of shortest retention time was found by n.m.r. spectroscopy and mass spectrometry to be methyl 2-methyl-6-(trifluoromethyl)benzoate.

Such complete and consecutive cleavage of fluorine from trifluoromethyl groups is usually rationalised in terms of decreasing bond strengths and progressively easier cleavage of carbon-fluorine bonds remaining after individual fluorine atoms are replaced by hydrogen. The observed order of bond lengths,¹¹ *i.e.* $\text{F}_2\text{C-F} < \text{HFC-F} < \text{H}_2\text{C-F}$, supports this view.

Voltammetry.—The ease of reduction in methanol solution is reflected in the potentials at which macro-scale

¹¹ L. Pauling, 'The Nature of the Chemical Bond,' Cornell Univ. Press, Ithaca, 1960, p. 314.

electrolysis proceeds at a convenient rate (Table 1) and these potentials do not point to any great difference in the

TABLE 4

Polarography in dimethylformamide solution ^a

Substrate	$E_1(\text{I})^b$	$E_1(\text{II})^b$	$i(\text{I})/i(\text{II})^c$
<i>p</i> -MeO ₂ CC ₆ H ₄ CH ₂ OMe	-1.61	-1.78	1.50
<i>p</i> -MeO ₂ CC ₆ H ₄ CH ₂ OAc	-1.39	-1.78	1.50
<i>p</i> -MeO ₂ CC ₆ H ₄ CF ₃	-1.26	-1.80	2.27
<i>m</i> -MeO ₂ CC ₆ H ₄ CF ₃	-1.40		
2,4-(CF ₃) ₂ C ₆ H ₃ CO ₂ Me	-0.98	-1.60	1.75
<i>p</i> -MeO ₂ CC ₆ H ₄ CH ₃		-1.74	
<i>m</i> -MeO ₂ CC ₆ H ₄ CH ₃		-1.77	

^a Dimethylformamide, Bu₄NI (0.1M), substrate *ca.* 3 × 10⁻⁴M.

^b V vs. Ag-AgI; (I) first wave; (II) second wave. ^c Ratio of wave heights.

ease of cleavage of the acetate, ether, or carbon-fluorine linkages.

interest that the 2,4-bis(trifluoromethyl) compound gives in acetonitrile, reversible one-electron reduction at relatively low sweep rates. This lends substance to the view that the corresponding radical anions are likely intermediates and that fluoride ion loss is slow when the conjugation of the methoxycarbonyl group with the ring is disturbed. In methanol solution hydrogen-bonded solvation of the fluoride ion must be a powerful driving force for fluoride ion expulsion from the radical ion. The cathodic reduction of trifluoromethyl groups in aprotic solvents is under investigation.

EXPERIMENTAL

Materials.—*p*-Methoxycarbonylbenzyl acetate, *p*-methoxycarbonylbenzyl methyl ether, and phenacyl acetate were prepared by minor modification of literature methods. The monotrifluoromethyl substituted compounds were prepared by standard methods according to Scheme 3.

TABLE 5

Cyclic voltammetry in acetonitrile solution ^a

Substrate	Peak potential (V vs. s.c.e.)	Peak current ^c (μA)	Sweep rate (mV s ⁻¹)
7,7,8,8-Tetracyanoquinodimethane ^b	+0.2	80	67
	+0.19	125	170
	+0.19	170	240
<i>p</i> -MeO ₂ CC ₆ H ₄ CF ₃	-1.88	187	67
	-1.93	306	170
	-1.95	463	240
2,4-(CF ₃) ₂ C ₆ H ₃ CO ₂ Me	-1.69	125	67
	-1.71	150	170 ^d
	-1.71	190	240 ^d

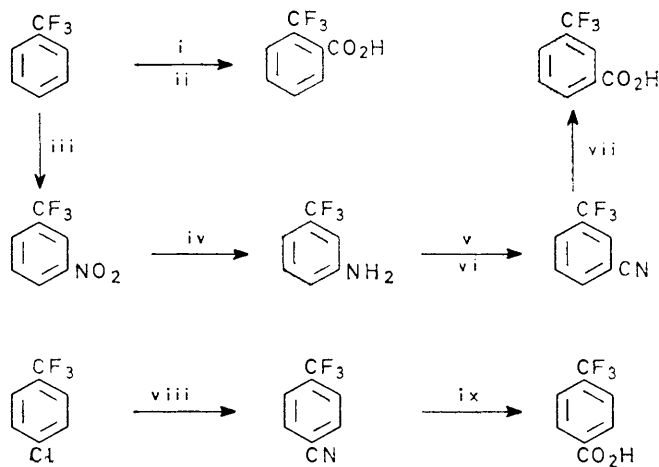
^a Gold disc cathode, substrate *ca.* 10⁻³M in acetonitrile-Bu₄NClO₄ (0.1M). ^b Known to give reversible one-electron reduction in acetonitrile (D. S. Acker and W. R. Hertler, *J. Amer. Chem. Soc.*, 1962, **84**, 3370). ^c Normalised for concentration of 1mm. ^d Voltammogram indicates partial reversibility.

The fact that the very strong carbon-fluorine bond is cleaved at least as easily as the carbon-oxygen bonds of the acetate and ether is powerful evidence against alternative mechanisms involving direct displacement at the benzylic carbon with the cathode acting as a nucleophile.

Differences in the ease of reduction can be seen however from the results of polarographic experiments using dimethylformamide solutions (Table 4). The influence of the highly electron-withdrawing trifluoromethyl group is evident, the most easily reduced substrate being the 2,4-bis(trifluoromethyl) compound. However, following the initial electron transfer there is in dimethylformamide solution a marked difference in the behaviour of the acetate and ether *vis à vis* the trifluoromethyl compounds. From Table 4 it can be seen that the ratios of limiting currents for the first (substrate) and second (product) waves fall somewhat short of the expected value of 2.0 for the acetate and ether and unacceptably short of the value of 6.0 expected for complete cleavage of a trifluoromethyl group.

The results (Table 5) of cyclic voltammetric experiments in which peak currents were compared with a standard confirm that in another aprotic solvent, acetonitrile, methyl *p*-(trifluoromethyl)benzoate is reduced irreversibly but in two electron process. It is also of

Bis(trifluoromethyl) Compounds.—The preparation of these compounds depended on the relative rates of esterification of the isomeric acids.



SCHEME 3

Reagents: i, BuLi; ii CO₂; iii HNO₃-H₂SO₄; iv, Fe-HCl; v, HNO₂; vi, CuCN; vii, H₂SO₄; viii, CuCN in *N*-methylpyrrolidone; ix, NaOH.

2,4- and 2,6-bis(trifluoromethyl)benzoic acid. Reaction of 1,3-bis(trifluoromethyl)benzene with butyl-lithium. Butyl-

lithium solution (300 ml, 0.21 mol) was filtered through glass wool and 1,3-bis(trifluoromethyl)benzene (43 g, 0.20 mol) was added. The solution was boiled under reflux for 2 h, then poured onto crushed Cardice (1500 g) and left to evaporate overnight. Sodium chloride (50 g) in water (300 ml) was added and the mixture was washed with ether (2 × 200 ml). The aqueous layer was acidified with conc. hydrochloric acid, giving a heavy yellow oil which was extracted into ether (2 × 200 ml). The combined ether extract was washed with water (100 ml), dried (MgSO₄), filtered and evaporated to leave a pale yellow solid (31.5 g). A sample of the crude product was esterified with diazomethane in ether and analysed by g.l.c. (F11, D.E. 207, 125°, p_N , 15 lb in⁻²). Three components were present (Table 6).

TABLE 6

Components from carboxylations and esterification of 1,3-bis(trifluoromethyl)benzene

Component	Retention time (min)	Rel. peak area
(1)	1.5	26
(2)	3	169
(3)	4.5	105

Separation of isomers. The crude product (31.5 g) was dissolved in methanol (600 ml) and conc. sulphuric acid (12 ml), and the solution was boiled under reflux for 120 h. Methanol was removed on the rotary evaporator and water (400 ml) was added. The mixture was shaken with ether (3 × 100 ml) and the combined ether extract was washed with saturated sodium hydrogen carbonate solution (3 × 75 ml) and water (50 ml), dried (MgSO₄), filtered, and evaporated to leave a liquid residue (13.7 g). The sodium hydrogen carbonate washings were acidified with conc. hydrochloric acid to give a yellow oil which was extracted into ether (2 × 100 ml). The combined ether extract was treated as above to give a pale yellow solid (10.4 g). The neutral fraction was again analysed by g.l.c. and was found to contain only component (1) (5%) and component (2) (95%). The acid fraction was esterified with diazomethane solution in ether, and analysed by g.l.c. as above. Only component (2) (5%) and component (3) (95%) were present. The acid fraction was recrystallised from light petroleum (b.p. 80–100°) to give 2,6-bis(trifluoromethyl)benzoic acid as needles (yield 7.7 g) (pure by g.l.c.), m.p. 138–139°, ν_{\max} (Nujol mull) 2400–3700 (hydrogen bonded OH), 1720 (C=O), 1300, and 1220–1070 cm⁻¹ (C-F), δ [(CD₃)₂SO] 7.60–8.22 (m, aromatic) (Found: C, 41.9; H, 1.65; F, 44.6. C₉H₄F₆O₂ requires C, 41.85; H, 1.55; F, 44.2%).

The neutral fraction was distilled under reduced pressure to give methyl 2,4-bis(trifluoromethyl)benzoate (yield 11.6 g) (96% pure by g.l.c.), b.p. 97–98° at 14 mmHg, ν_{\max} (liquid film) 1740 (C=O), 1280, and 1180–1130 cm⁻¹ (C-F), δ (CCl₄) 3.97 (3H, s, OCH₃), and 7.87–8.13 (3H, m, aromatic) (Found: C, 44.2; H, 2.1; F, 41.5. C₁₀H₆F₆O₂ requires C, 44.1; H, 2.2; F, 41.9%).

Methyl 2,6-bis(trifluoromethyl)benzoate. The corresponding acid (7.7 g) was dissolved in ether (25 ml) and esterified with ethereal diazomethane solution in the usual way. The resulting yellow oil was distilled under reduced pressure (yield 7.6 g, 94%), b.p. 96–97° at 13 mmHg, m.p. 30–31°, ν_{\max} (Nujol mull) 1740 (C=O) and 1220–1070 cm⁻¹ (C-F), δ (CCl₄) 3.95 (3H, s, OCH₃) and 7.48–8.07 (3H, m, aromatic)

(Found: C, 44.05; H, 2.15; F, 42.3. C₁₀H₆F₆O₂ requires C, 44.1; H, 2.2; F, 41.9%). G.l.c. analysis, as above, showed only component (3).

2,4-Bis(trifluoromethyl)benzoic acid. The corresponding ester (0.99 g) was added to potassium hydroxide (3.5 g) dissolved in ethanol (5 ml) and water (1.5 ml). The solution was boiled under reflux for 24 h. The reaction mixture was worked up in the usual way to give a solid (0.92 g). Recrystallisation from light petroleum (b.p. 80–100°) gave leaflets (yield 0.62 g, 70%), m.p. 111–112°, ν_{\max} (Nujol mull) 2400–3200 (hydrogen bonded OH), 1720 (C=O), 1280, and 1170–1120 cm⁻¹ (C-F), δ [(CD₃)₂SO] 8.03–8.17 (m, aromatic) (Found: C, 41.6; H, 1.5; F, 44.5. C₉H₄F₆O₂ requires C, 41.85; H, 1.55; F, 44.2%).

Assignment of structures. Structures were assigned to the two major components (2) and (3) on the basis of relative rates of esterification of the acid, and on ¹⁹F n.m.r. spectra.

Component (2). This was formed by esterification of the crude acid with methanol–sulphuric acid, ¹⁹F n.m.r. (94.075 MHz, CCl₄, peaks quoted as p.p.m. upfield from CFC1₃). 60.86 (s, relative intensity 80), 63.88 (s, 13), and 64.14 (s, 80).

Component (3). This was not formed by esterification in methanol, only by treatment with diazomethane, ¹⁹F n.m.r. (as above) 60.80 (s). On the basis of this evidence, component (2) was concluded to be methyl 2,4-bis(trifluoromethyl)benzoate, formed from the corresponding acid. Component (3) was concluded to be methyl 2,6-bis(trifluoromethyl)benzoate, formed from the corresponding acid. Component (1) is probably the third isomer, methyl 3,5-bis(trifluoromethyl)benzoate.

Preparative Scale Electrolyses.—An undivided, water jacketed cell was used which was equipped with a magnetic stirrer and provision for the mounting of rectangular electrodes at ca. 3 mm separation. The reference electrode (s.c.e.) was in contact with the working electrode *via* an agar tetramethylammonium chloride bridge. For controlled potential electrolysis a Chemical Electronics TR70/2A potentiostat was used. For constant current electrolysis a stabilised d.c. power supply (Coutant Electronics Ltd.) was used and the electrode potential was monitored with a Y-t chart recorder.

Analytical Procedures.—G.l.c. was carried out using either Perkin-Elmer F11 or Varian Aerograph A90P instruments. Relative peak areas were measured using a Kent Chromalog integrator or by tracing and weighing. To enable quantitative determinations of yields to be made known amounts of suitable standard compounds were added to crude product mixtures. The response factors for the various starting materials, products, and internal standards had previously been measured. Authentic samples of electrolysis products were prepared by established methods.

T.l.c. Analysis of p-Methoxycarbonylbenzyl Methyl Ether Reduction Products.—The products of controlled potential electroreduction at both lead and mercury cathodes (Table 1) were analysed by t.l.c. using silica plates (HF 254) eluted with light petroleum (b.p. 40–60°)–benzene–acetone 85:10:5. An authentic sample of 4,4'-bis(methoxycarbonyl)bibenzyl, run on the same plate, did not correspond to any of the compounds in the electrolysis products.

Rotating Lead Disc Electrode.—A conventional rotating electrode assembly (Beckmann) was fitted with a Teflon cylinder with a copper core which was recessed at one end to accommodate a press fitted lead plug (diam. 5 mm).

Voltammetry.—A Heathkit polarography module equipped

with a Hewlett-Packard 7035B X-Y recorder was used for cyclic voltammetry at a gold disc cathode (Beckmann 39087). Solutions were *ca.* 10^{-3}M in acetonitrile containing tetrabutylammonium perchlorate (0.1M).

Polarographic experiments used *ca.* $3 \times 10^{-4}\text{M}$ solutions in dimethylformamide containing tetrabutylammonium iodide the instrument being a Radiometer Polariter type PO4.

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