Anodic Oxidation. Part XI.[1] Carbon Anodes in Electrosyntheses based on Carboxylate Ions

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Preparative electrolyses of triethylammonium heptanoate using different types of carbon as the anode material are reported. In protic solvents dodecane, the Kolbe dimer, is the major product at vitreous or baked carbon anodes, but the major products at a graphite anode are the three hexyl heptanoates. Large differences in the product distribution between electrolyses using anodes constructed from the edge and the face surfaces of pyrolytic graphite lead to the view that the differences amongst all the types of carbon are due to their differing adsorptive properties. Additional examples of the Kolbe electrosynthesis at vitreous and baked carbon anodes are reported.

The electrochemical oxidative decarboxylation of aliphatic carboxylate ions can lead either to coupled products, as in the Kolbe electrosynthesis, or to the so-called Hofer–Moest products; for example acetate ion can be converted, depending on the conditions, predominantly into either ethane, or into methyl acetate.[2] Although the mechanistic details are still not fully understood it is now recognised that the Kolbe dimers are formed from radical intermediates, whereas Hofer–Moest products are formed through cationic intermediates.[2] The influence of the electrode material on the nature of the products is one important and still outstanding problem. The formation of Kolbe dimers in aqueous solution normally requires the use of a smooth platinum or iridium anode [2] although some ethane is produced in the electrolysis of acetate ion at an ' arc carbon ' electrode.[3] With graphite anodes the predominant products are usually of the Hofer–Moest type, although it has recently been shown that ' unmachined amorphous graphite ' alone out of a variety of graphite anode materials promotes the formation of Kolbe dimers in aqueous acetonitrile.[4] The anode material is less critical in non-aqueous solvents [2] but nearly all preparative Kolbe electrosyntheses have been performed using a smooth platinum anode, although Kolbe dimer formation has been reported in methanol for some substituted carboxylates with anodes of sealed graphite,[5] charcoal,[6] and an unspecified form of carbon.[7] We report here, first, our results showing the extent to which each of three anodes of different types of carbon promotes the formation of the Kolbe dimer in the electrochemical oxidative decarboxylation in protic solvents of a typical carboxylate ion, heptanoate ion.

Heptanoic acid, partly neutralised by triethylamine, and solutions of heptanoic acid, partly neutralised by triethylamine, in water, methanol, ethanol, and *NN*-dimethylformamide were electrolysed at an approximately constant current using a carbon anode and a platinum cathode in an undivided preparative-scale cell,

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and the chemical yields of the Kolbe dimer, dodecane, were determined. The materials used to construct the anodes were a commercial soft graphite, two hard carbons, vitreous carbon,[8] and baked carbon which is a gas-coke type of carbon and is the intermediate stage between the carbonisation and graphitisation steps in the manufacture of the graphite. The results, together with comparable figures for electrolyses at a platinum anode, are shown in Table 1. The use of either of the hard carbon anodes led to substantial yields of the Kolbe dimer in protic solvents. The major products from the electrolyses with a graphite anode in the protic solvents were shown to be hexyl, 1-methylpentyl, and 1-ethylbutyl heptanoates by g.l.c. comparison with authentic samples using an FFAP column. On many analytical columns separation of the 1-methylpentyl and 2-ethylbutyl heptanoates was not possible. The presence of hexyl heptanoate was confirmed by a comparison of the n.m.r. spectrum of a sample isolated by preparative g.l.c. with that of an authentic sample, and the presence of 1-methylpentyl and 1-ethylbutyl heptanoates by the identification of hexan-2-ol and hexan-3-ol amongst the products of the alkaline hydrolysis of the electrolysis products through a comparison with authentic samples based on g.l.c. retention times. Hexyl and 1-methylpentyl heptanoates, but not 1-ethylbutyl heptanoate were reported[9] amongst the products of an electrolysis of potassium heptanoate in the presence of high concentrations of potassium carbonate and potassium hydrogen carbonate in water at a platinum electrode. However, the formation of hexan-3-ol as well as hexan-1-ol and hexan-2-ol in the nitrous acid deamination of 1-aminohexane in aqueous solution[10] shows that the hexyl cation rearranges to both the 1-methylpentyl and the 1-ethylbutyl cations, so that the presence of 1-ethylbutyl heptanoate in our electrolysis products was expected. The major product from the electrolysis using a vitreous carbon anode in *NN*-dimethylformamide was collected by semi-preparative g.l.c. and identified by elemental analysis and i.r. and n.m.r. spectroscopy as *N*-heptanoyloxymethyl-*N*-methylformamide; the major product using a platinum anode is dodecane. In the protic solvents the major product using either of these anodes is dodecane, and this difference in behaviour in *NN*-dimethylformamide is surprising. The formation of *N*-acyloxymethyl-*N*-methylformamides as the major products when carboxylic acids are electrolysed at a platinum anode in *NN*-dimethylformamide in the presence of a variety of supporting electrolytes is well known,[11] but the formation of substantial amounts of the Kolbe dimer has also been reported[12] for the electrolysis of some triethylammonium carboxylates in *NN*-dimethylformamide using a platinum anode.

TABLE 1

Electrolyses of heptanoic acid.[a] Chemical yields (%)[b] of dodecane

	Anode			
Solvent	Graphite	Vitreous carbon	Baked carbon	Platinum[c]
MeOH	1	24—33[d]	30	52
EtOH	5—9[d,e]	45—53[d]	39	62
H_2O	2	47—50[d]		45
$Me[CH_2]_5CO_2H$[f]	1	33		
$HCONMe_2$	0	1—3·5[d,g]		66

[a] Heptanoic acid (0·02M) was neutralised to the extent of 20% by triethylamine; *apparent* current density, 110–65 mA cm^{-2} (vitreous carbon) 11 mA cm^{-2} (baked carbon and graphite). [b] Based on unrecovered starting acid, and obtained by quantitative analysis using g.l.c. with calibration against dodecane. [c] From G. B. Cox, Ph.D. Thesis, Sheffield, 1968, 0·01M solutions; current density, 300–40 mA cm^{-2}. [d] Results from a number of duplicate experiments fell within these limits. [e] The major products were hexyl, 1-methylpentyl, and 1-ethylbutyl heptanoates. [f] The electrolyte consisted of heptanoic acid (150 ml, 1·15 mol) and triethylamine (17 ml, 0·125 mol); *apparent* current density, 15 mA cm^{-2} (vitreous carbon), 5 mA cm^{-2} (graphite). [g] The major product was *N*-heptanoyloxymethyl-N-methylformamide.

Since the results with heptanoic acid (Table 1) showed that the two hard carbon electrodes gave substantial yields of the Kolbe dimer in protic solvents the work was then extended to some substituted acids, *viz.*, phenylacetic and phenoxyacetic acids and ethyl and methyl hydrogen succinates. The earlier results led to the choice of ethanol as the solvent, except for the methyl half-ester where methanol was used to avoid the possibility of transesterification; pyridine was used as a co-solvent with the two aromatic acids, since previous work[13,14] using both platinum and carbon electrodes had shown that this prevented coating of the electrode by polymeric material. The results are shown in Table 2. Again substantial amounts of the Kolbe dimers are formed at the hard carbon electrodes, even in the case of the α-substituted acids where the relatively low oxidation potentials of the benzyl and phenoxymethyl radicals might be expected to favour the formation of products derived from cationic intermediates. It had earlier been reported[14] that electrolyses of phenylacetic acid in aqueous or methanolic pyridine at an electrode made of an unspecified type of carbon produced none of the Kolbe dimer. Our results suggest that the anode in that case was of graphite. The use of a platinum anode[13-15] leads, as with a vitreous carbon anode, to substantial amounts of the Kolbe dimer. The divergence in behaviour between a platinum and a carbon anode in the electrolysis of phenylacetic acid has been attributed to the presence within the carbon of paramagnetic centres, which by binding the initially formed radicals impede their desorption and

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promote a second electron transfer.[14] Whilst it is very probable that adsorption plays an important part in determining whether radical- or cation-derived products are formed[15] we feel that this particular suggestion must be rejected since it cannot explain the differences in behaviour which we have observed between baked carbon and graphite, which in view of their common origins are both likely to contain paramagnetic impurities at the surface. Another related factor which is recognised to have an effect on the course of the electrolysis of carboxylates[2] is the current density. In the electrolyses listed in Tables 1 and 2 the current was chosen to allow sufficient product to be formed on a preparative scale within a reasonable time, thus leading to differences in the *apparent* current densities between the vitreous carbon anode on the one hand and the baked carbon and graphite anodes on the other.

TABLE 2

Electrolyses of carboxylic acids.[a] Chemical yields (%)[b] of the Kolbe dimer

		Anode		
Acid	Solvent	Graphite	Vitreous carbon	Baked carbon
$PhCH_2CO_2H$	EtOH–C_5H_5N[c]	0	45[d]	
$PhOCH_2CO_2H$	EtOH–C_5H_5N[c]	6	23—25[e]	
$MeO_2C(CH_2)_2CO_2H$	MeOH	1	21	15
$EtO_2C(CH_2)_2CO_2H$	EtOH	20	37	38

[a] The aromatic acid (0·02M) or the half-ester (0·01M) was neutralised to the extent of 20% with triethylamine; *apparent* current density, 90 mA cm^{-2} (vitreous carbon), 11 mA cm^{-2} (baked carbon and graphite). [b] Based on unrecovered starting acid and obtained by direct isolation of part of the Kolbe dimer together with quantitative analysis using g.l.c. of the remainder of the material with calibration against the Kolbe dimer. [c] Ethanol–pyridine (2 : 1, v/v). [d] Other products included benzyl ethyl ether, benzyl phenylacetate, and (traces of) ethyl phenylacetate. [e] Other products included ethyl phenoxyacetate and phenol.

In order to obtain more information about the importance of surface properties at a carbon anode in determining the nature of the products we have investigated the electrolysis of heptanoic acid, partly neutralised with triethylamine, in ethanol using two different anodes of pyrolytic graphite.[8] Pyrolytic graphite, a very pure form of carbon, is strongly anisotropic because of the orientation of the atomic planes within the crystal. Marked differences in electrochemical behaviour, for example in the hydrogen evolution reaction[16] and in the oxidation of the hydroperoxide anion,[17] have been observed for pyrolytic graphite electrodes depending on whether the electrode surface is parallel (pyrolytic face) or perpendicular (pyrolytic edge) to a cleavage plane. In our experiments it was found that at least 80% of the product formed when a pyrolytic edge electrode was used was the Kolbe dimer, dodecane, but that at a pyrolytic face electrode the proportion of dodecane in the products dropped to 27% and 60% of the products consisted of the three C_6 heptanoates. The apparent current density, 320 mA cm^{-1}, was the same in the two cases, but the actual current density may be *ca.* 10 times less for the pyrolytic edge electrode than for the pyrolytic face electrode due to the relative roughnesses of the two surfaces.[16] The formation of the Kolbe dimer is usually favoured by a high current density,[2] which may be part of the explanation of why a vitreous carbon anode leads to higher yields of the Kolbe dimer than a graphite anode in the electrolyses listed in Tables 1 and 2, but some other explanation for our results at the pyrolytic graphite electrodes is necessary. The number of adsorption sites is much greater for a pyrolytic edge electrode[17] and we conclude that the behaviour of such an electrode in promoting the formation of the radical-derived Kolbe dimer is due to the greater concentration of adsorbed radical intermediates at such an electrode, which should favour the bimolecular dimerisation process over the alternative process of further oxidation to the cation. That smooth platinum, vitreous carbon, and baked carbon electrodes are all more successful than soft graphite electrodes in promoting the formation of the Kolbe dimer can likewise be attributed to the greater number of adsorption sites in electrodes of the first group. The conclusions are compatible with a recent discussion on the ratio of radical- to cation-derived products in the electrolyses of a series of phenylacetate ions at a platinum electrode.[15] The differences in the extent to which absorption occurs at the two types of pyrolytic graphite electrode would also be expected to affect the potential required for the discharge of heptanoate ions at these electrodes, and with this in mind we have attempted to measure these potentials in ethanol by making polarisation curve measurements. Unfortunately under conditions corresponding to those in our preparative electrolyses, even when problems due to the formation of polymeric films at the electrode surface had been overcome, it was not possible to carry out voltammetric studies due to the low conductivity of the system. Voltammetric studies of the discharge of carboxylate ions at pyrolytic graphite or other carbon electrodes could be carried out under other conditions, but the results could not then be related to our preparative experiments.

Our work clearly shows that anodes of vitreous carbon, appropriately orientated pyrolytic graphite, and also the cheap baked carbon, but not soft graphite, can be used successfully in the Kolbe electrosynthesis.

EXPERIMENTAL

N.m.r. spectra were recorded on Varian A60 or HA100 instruments in $CDCl_3$, with tetramethylsilane as internal standard. The integrations were in every case in agreement with the proton assignments. I.r. spectra were measured on a Perkin-Elmer 137 spectrophotometer.

Starting Materials and Reference Compounds.—Heptanoic acid (B.D.H.) was redistilled before use. Phenoxyacetic

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acid, m.p. 98—99° (lit.,[18] 99°), methyl hydrogen succinate, m.p. 56—58° (lit.,[19] 57—58°) and ethyl hydrogen succinate, b.p. 134—138° at 10 mmHg (lit.,[20] 146—149° at 17 mmHg) were prepared by standard methods. Dodecane was supplied by Dr. J. G. Parkin [21] and had b.p. 210—212° at 754 mmHg, n_D^{21} 1·4201 (lit.,[22] 216·2° at 760 mmHg,[23] n_D^{20} 1·4219). C_6 Heptanoates were prepared from the corresponding alcohols and heptanoyl chloride. Hexyl heptanoate had b.p. 122—125° at 9 mmHg (lit.,[24] 137° at 19 mmHg), τ 5·82 (t, J 6·5 Hz, CH_2O), 7·62 (t, J 6·5 Hz, CH_2CO), 8·2—8·8 (c, 8 × CH_2), and 9·1 (t, J 6·5 Hz, 2 × Me), 1-methylpentyl heptanoate had b.p. 108—110° at 9 mmHg, n_D^{20} 1·4238 (lit.,[25] 127° at 17 mmHg, n_D^{20} 1·4240), τ 5·1 (sext., CHO), 7·73 (t, J 6·5 Hz, CH_2CO), 8·2—8·8 (c, 7 × CH_2), 8·75 (t, J 6·5 Hz, CH_3CHO), and 9·12 (t, J 6·5 Hz, 2 × Me), and 1-*ethylbutyl heptanoate* had b.p. 120° at 24 mmHg, τ 5·28 (quint., CHO), 7·84 (t, J 7 Hz, CH_2CO), 8·5—8·9 (c, 7 × CH_2), and 9·20 (c, 3 × Me) (Found: C, 72·9; H, 12·0%; *M*, 214·1936. $C_{13}H_{26}O_2$ requires C, 72·9; H, 12·15%; *M*, 214·1933). Ethyl phenylacetate, b.p. 108—109° at 13 mmHg (lit.,[26] 110° at 17 mmHg), benzyl ethyl ether, b.p. 180—182° (lit.,[27] 185°), τ 2·90 (s, Ph), 5·72 (s, $PhCH_2$), 6·70 (q, J 7 Hz, CH_2Me), and 8·95 (t, J 7 Hz, Me), benzyl phenylacetate, b.p. 316—320° (lit.,[28] 317—319°), τ 2·82 (s, 2 × Ph), 5·01 (s, CH_2O), and 6·50 (s, CH_2CO), ethyl phenoxyacetate, b.p. 128—130° at 13 mmHg (lit.,[18] 140—144° at 24 mmHg), phenyl toluene-*p*-sulphonate, m.p. 94—95° (lit.,[29] 94—95°), and dimethyl adipate, b.p. 125—126° at 24 mmHg, n_D^{21} 1·4283 (lit.,[30] 120·5° at 17 mmHg, n_D^{20} 1·4283), τ 6·35 (s, 2 × Me), 7·70, and 8·40 (m, 4 × CH_2) were prepared by standard methods.

Electrolyte Cells.—Preparative electrolyses were conducted in a simple undivided cell of 500 ml capacity fitted with an internal cooling coil and either a mechanical or a magnetic stirrer. A rectangular platinum cathode (2·0 × 2·9 cm) was separated from the anode by *ca.* 0·5 cm. Vitreous carbon anodes were constructed from cylindrical rods of vitreous carbon (Vitreous Carbons Ltd.) 0·4 cm in diameter and 5 cm in length. Electrical contact was maintained by electroplating one end of the rod with copper and soldering a lead onto the copper; that end of the rod was then sealed into a glass tube with 'Araldite.' During electrolyses the vitreous carbon was immersed in the electrolyte to a depth of 3·5 cm. Graphite (British Acheson Electrodes Ltd., grade AGLR) and baked carbon (British Acheson Electrodes Ltd.) anodes were cylindrical in form with a diameter of 1·8 cm and a length of 10 cm. They were drilled and tapped at one end and a heli-coil screw-thread insert (2BA × 2½D) was introduced into which a brass terminal pillar (2BA) was then fitted with a beryllium–copper wavy washer under the head of the terminal pillar to provide maximum electrical contact with the carbon. During electrolyses the carbon was immersed in the electrolyte to a depth of 6 cm. Anodes of pyrolytic graphite were constructed from cylinders of pyrolytic graphite (Le Carbone Ltd.) in which the appropriate face or edge surface orientation was exposed at the ends of the cylinders. The curved surfaces of the cylinders were then sealed by enclosing them in 'Flo-Tite' heat shrink polytetrafluoroethylene tubing (Pope Scientific Inc., U.S.A.). One end of the cylinder was electroplated with copper, to which an electrical lead was soldered, and the other end, with a surface area of 0·44 cm² was immersed in the electrolyte. The platinum and vitreous carbon electrodes were cleaned prior to each electrolysis by scouring them and then washing them with water and then acetone. The baked carbon and graphite electrodes were soaked for 24 h in chloroform, washed in ether, and dried at 100° before each electrolysis. Polymeric material was removed by scraping before each cleansing operation.

Electrolyses.—All preparative electrolyses were performed according to the following general scheme, with only slight departures from the procedure in individual cases.

The carboxylic acid (0·1 mol) and triethylamine (3 ml) were dissolved in the solvent (200 ml) and the solution was electrolysed at 18—23° using a 100 V d.c. supply. The current was kept constant by manual adjustment of the resistance in the circuit and 1·5 equiv. of charge was passed. The crude product mixture was then neutralised with acetic acid and the solvent distilled. The residue was poured into water (200 ml) and extracted with ether (3 × 100 ml). The combined ether extracts were then washed with 1N-sodium hydroxide (100 ml) and water (3 × 100 ml) and dried (Na_2SO_4). The alkaline washings were reacidified with acetic acid, extracted with ether (3 × 100 ml), and these combined extracts were dried (Na_2SO_4). The ether was removed from both sets of combined extracts on a rotary evaporator and the residues were distilled. Distillation fractions were then analysed qualitatively and quantitatively by g.l.c. Chemical yields (Table 1) are based on unrecovered starting acid. In electrolyses in excess of heptanoic acid as solvent a much greater proportion of triethylamine (17 ml) was used to provide a measurable current owing to the low conductivity of this solvent. In electrolyses with aromatic acids a mixed solvent, ethanol–pyridine (2 : 1; v/v), was used. Electrolyses with alkyl hydrogen succinates were performed on a 0·05 molar scale using the same volume (200 ml) of solvent. The electrolyses using pyrolytic graphite anodes were performed on a smaller scale. For the experiment with a pyrolytic face anode the electrolyte consisted of heptanoic acid (2·5 g) and triethylamine (1·0 ml) in ethanol (150 ml) and for the pyrolytic edge anode heptanoic acid (1·6 g) and triethylamine (1·0 ml) in ethanol (40 ml). During the latter electrolysis manual cleaning of the anode was necessary several times during the course of the electrolysis.

G.l.c.—Quantitative g.l.c. was mainly performed on a Perkin-Elmer F 11 instrument fitted with a disc integrator. A few analyses were also carried out using a Griffin and George D 6 instrument having a gas density balance and on an F and M 810 instrument. Qualitative g.l.c. was performed on these instruments and also on an F and M 720 instrument. Identifications of products based solely on the comparison of retention times on g.l.c. with those of authentic samples were always based on measurements

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made on more than one column and on more than one instrument. Quantitative chemical yields (Tables 1 and 2) were calculated from measurements of relative peak areas combined with calibrations against reference samples. Semi-preparative g.l.c. was performed on an F and M 720 instrument and preparative g.l.c. on a Varian Aerograph A 700 instrument.

Identification of Products from Electrolyses with Heptanoic Acid.—Preparative g.l.c. on material, b.p. 90—120° at 20 mmHg, from an electrolysis of triethylammonium heptanoate in methanol at a vitreous carbon anode (A 700; 10′; silicone rubber; 150°) and semi-preparative g.l.c. on material, b.p. 110—118° at 14 mmHg, from an electrolysis of triethylammonium heptanoate in ethanol at a graphite anode (F and M 720; 2′; 10% silicone oil; 150°) gave dodecane identified by spectroscopic comparison with an authentic sample. Examination of the products from an electrolysis of triethylammonium heptanoate in ethanol at a graphite anode by g.l.c. (F 11; 6′; FFAP; 90° for 45 min, then programmed at 5° min^{-1}; N_2 carrier gas at 40 ml min^{-1}) showed the presence of dodecane and C_6 heptanoates having retention times of 4, 36, 39, and 54·5 min, respectively, identical with those of authentic samples as confirmed by peak enhancement studies, together with two unidentified products having retention times of 9 and 56·5 min. Hexyl, 1-methylpentyl, and 1-ethylbutyl heptanoates, the major products, were present in the ratio 1 : 2·5 : 2·25. Hexyl heptanoate, spectroscopically identical with an authentic sample, was collected by semi-preparative g.l.c. (F and M 720; 2′; 10% silicone oil; 150°) but under these conditions the other two esters could not be collected separately. The products (3·5 g) were hydrolysed by heating them under reflux for 6 h with 1N-sodium hydroxide (25 ml). Examination of the neutral hydrolysis products by g.l.c. (F and M 810; 4′, 10% Carbowax 400; 100°; N_2 carrier gas at 50 ml min^{-1}) showed the presence of hexan-3-ol, hexan-2-ol, and hexan-1-ol having retention times of 5·5, 6·5, and 13·5 min, respectively, identical with those of authentic samples as confirmed by peak enhancement studies. N-*Heptanoyloxymethyl*-N-*methylformamide*, τ 1·7 (s, CH=O), 4·75 (s, $OCH_2N=$), 7·11 (s, NMe), 7·72 (t, *J* 7 Hz, CH_2CO), 8·2—8·8 (c, 4 × CH_2), and 9·1 (t, *Me*CH_2), $\nu_{max.}$ 1745 and 1695 (both C=O) cm^{-1} (Found: C, 59·8; H, 9·5; N, 6·9%; *M*, 201. $C_{10}H_{19}NO_2$ requires C, 59·7; H, 9·45; N, 7·0%; *M*, 201) was obtained by semi-preparative g.l.c. (F and M 720; 2′; 10% Apiezon; 180°) on a fraction b.p. 175—192° (bath) at 16 mmHg from the electrolysis of triethylammonium heptanoate at a vitreous carbon anode.

Identification of Products from the Electrolysis of Phenylacetic Acid.—The major fraction, b.p. 140—150° at 13 mmHg, from the electrolysis of triethylammonium phenylacetate at a vitreous carbon anode crystallised, and recrystallisation from acetone–ethanol (4 : 1) gave bibenzyl, m.p. and mixed m.p. 51—51·5°. Analysis by g.l.c. of fractions b.p. 90—120 and 150—190° at 13 mmHg showed the presence in addition to bibenzyl of benzyl ethyl ether, benzyl phenylacetate, and traces of ethyl phenylacetate.

Identification of Products from the Electrolysis of Phenoxyacetic Acid.—The neutral products from an electrolysis of triethylammonium phenoxyacetate at a vitreous carbon anode on crystallisation from ethanol afforded 1,2-diphenoxyethane, m.p. 98—99° (lit.,[30] 98°), τ 2·5—3·15 (c, 2 × Ph) and 5·65 (2 × CH_2). Examination of the material recovered from the mother liquors, by g.l.c., showed the presence of ethyl phenoxyacetate, a sample of which was isolated by semi-preparative g.l.c. (F and M 720; 2′; 10% silicon oil; 150°) and identified by spectroscopic comparison with an authentic sample. Phenol, characterised as phenyl toluene-*p*-sulphonate, m.p. and mixed m.p. 94—95°, was isolated from the acidic fraction.

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