Canadian Journal of Chemistry

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOLUME 44 DECEMBER 1, 1966 NUMBER 23

THE ELECTROLYSIS OF *o*-HALOGENOPHENYL-SUBSTITUTED ACIDS

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Received June 15, 1966

ABSTRACT

The synthesis and electrolysis of a series of *o*-chloro- and *o*-bromo-phenyl-substituted acids with two to five carbon chain lengths have been studied. The main products, under the experimental conditions used, were the Kolbe dimers. A complete isolation and identification of all of the important by-products is recorded. Methanol and methanol–pyridine were the solvents for electrolysis.

This work represents the first study of the behavior of aromatic halogen substituents during the Kolbe electrolysis. In contrast to many reactions involving aliphatic halogen substituents, no free halogen was produced and no products were obtained, even in trace amounts, where halogen had been lost from the aromatic nucleus. During this investigation, 18 previously unreported compounds were synthesized and their properties were determined.

Recently, there has been an increase in interest in the electrolysis reactions of aryl-substituted aliphatic acids (refs. 1–4 and articles cited therein). In part, this interest has involved efforts to observe other than normal Kolbe coupling reactions, and in particular to study phenyl migration in free radicals and homolytic cyclization of the radicals involved. No studies were undertaken with halogenated aromatic rings.

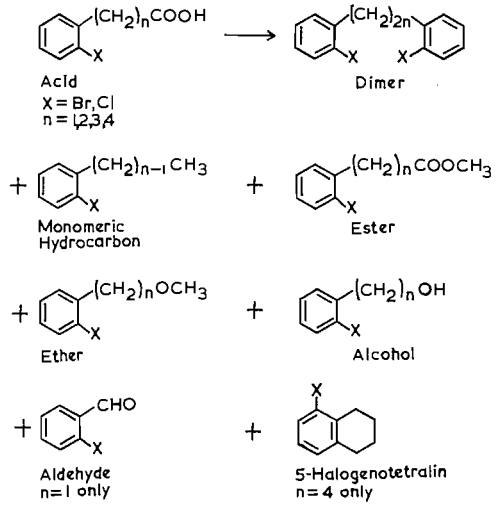
Past work (5, 6) has shown that halogen is readily lost during electrolysis of some ω-halogenated aliphatic acids. It was expected that halogen would be more stable and thus less easily lost from an aromatic ring than from an aliphatic chain. However, because of the complete lack of work in this area, it was felt worthy of investigation. As a start, efforts were concentrated on *o*-chloro- and *o*-bromo-phenyl-substituted acids of two to five carbon chain lengths. It was hoped to learn something of the radicals produced, their reactions, and to what extent this class of organic acids might be used in the synthesis of Kolbe-type halogenated hydrocarbons.

It is difficult to produce and separate large quantities of pure ortho isomers from the ortho–para mixture obtained on direct halogenation of an aromatic ring. Thus, the acids used were all synthesized from starting materials with the halogen substituent already on the ring.

Two new acids were prepared: 4-*o*-bromophenylbutanoic acid and 5-*o*-bromophenylpentanoic acid. All other acids had been synthesized previously. Misra and Shukla (7) prepared *o*-halogenated phenylacetic acids by reacting *o*-halogenated benzyl bromide and chloride with sodium cyanide; hydrolysis gave the desired acids. This method was used to prepare the necessary substituted acetic acids and extended to produce the halogenophenylbutanoic acids.

Various workers (8–11) have synthesized *o*-halogenophenylpropanoic acids from the corresponding *o*-halobenzyl halides and diethyl malonate, although not on the scale of reaction used in the present work. Granger (12) extended the method to prepare 5-*o*-chlorophenylpentanoic acid, but gave no experimental details. The necessary propanoic and pentanoic acids were prepared by this route.

The *o*-halogenophenyl-substituted acids were electrolyzed in methanol and methanol–pyridine solution. The products are illustrated in Reaction Scheme 1, and the yields are described in Table I.



REACTION SCHEME 1.

Previous electrolyses of *o*-substituted phenylacetic acids have indicated that the size of the ortho substituent is a very important factor in dimer formation. If the group is small, considerable dimer is formed; if the group is large, little or no dimer is formed. The best yield of dimer from the electrolysis of phenylacetic acid itself (i.e. when the ortho substituent is hydrogen) was 55% in methanol solvent (13) and 59% in dimethylformamide (4). Mesitylacetic acid (i.e. two *o*-methyl groups) gives (4) 44% dimer, and 2,4,6-triisopropylphenylacetic acid (i.e. two *o*-isopropyl groups) gives only 31% dimer (4). Wladislaw (2) found that the bulky nitro substituent in 2-nitrophenylacetic acid suppressed dimer formation completely; this was also true with nitro groups in the 2,4-positions, but with a 4-nitro substituent alone, 33% dimer was produced. However, this effect may not be entirely a steric one, since a 3-nitro substituent also suppresses dimer formation completely (Wladislaw concluded that more information was needed to justify any general discussion of how substituents influence the electrolysis products from substituted phenylacetic acids). In our work, an *o*-bromo substituent, which is relatively large, but still smaller than nitro, suppresses dimer formation but does not completely eliminate it. An *o*-chloro substituent, which is considerably smaller, allows more dimer formation, but still less than that with unsubstituted phenylacetic acid. Any steric hindrance vanishes once the chain length of the acid is increased by one carbon or more; this is borne out in most cases by the increased yields of dimer for the other *o*-halogenophenyl-substituted acids studied.

In the past, the Kolbe reaction of an acid RCOOH has been regarded usually as a relatively simple free-radical process involving the production, at the anode, of radicals

TABLE I

Electrolysis products from *o*-halogenophenyl-substituted acids

Acid used	Solvent†	Product yields (%)*							
		Dimer	Monomeric hydrocarbon	Ester	Ether	Alcohol	Aldehyde	5-Halogeno-tetralin	Unidentified polymer‡
o-Bromophenylacetic acid	M	3.4	—	6.1	10.0	—	7.8	—	40
o-Chlorophenylacetic acid	M	15.1	—	11.8	13.8	—	Trace	—	29
3-*o*-Bromophenylpropanoic acid	M	23.6	8.0	6.8	12.9	Trace	—	—	32
3-*o*-Chlorophenylpropanoic acid	M	25.2	10.3	7.4	17.0	—	—	—	21
4-*o*-Bromophenylbutanoic acid	M	14.0	10.5	15.0	9.4	1.3	—	—	27
4-*o*-Chlorophenylbutanoic acid	M	24.0	13.0	10.0	6.2	3.0	—	—	30
5-*o*-Bromophenylpentanoic acid	M	9.2	10.7	13.0	1.9	1.4	—	4.0§	45
5-*o*-Bromophenylpentanoic acid	M–P	22.6	10.9	8.3	6.2	1.8	—	6.2§	22
5-*o*-Chlorophenylpentanoic acid	M	10.2	9.8	9.0	4.6	4.7	—	7.0§	31
5-*o*-Chlorophenylpentanoic acid	M–P	28.8	12.8	6.7	2.1	0.9	—	3.5§	20

*Calculated in the usual manner based on the amount of acid reacting. The yields of unidentified polymeric fractions are based on a weight ratio exclusively (i.e. weight polymer/weight acid reacting) and hence cannot be regarded as accurate; they do give a good indication of the extent of polymer formation.

†M = methanol; M–P = methanol–pyridine.

‡The term polymer is used for convenience. The fraction consists of ether-insoluble material that settles on the electrodes during electrolysis plus the high-boiling, tarry residue left when the total neutral product is first distilled. Sodium fusion tests and infrared spectra showed the presence of halogen and ortho aromatic substitution in both components, but no further identification was made.

§No trace of unsubstituted tetralin was found.

RCOO· and R· and their subsequent reaction. In methanol solvent, oxidation of CH_3O^- or CH_3OH to CH_3O· has been an additional factor assumed to be important in product formation and subsequently confirmed (e.g. ref. 14 and articles contained therein). However, recent studies indicate that the Kolbe reaction is often a much more complicated process, or at least it has the potential to be so under the experimental conditions used. Where R· is a normal primary alkyl radical, the formation of products can be reconciled with radical intermediates; except under strong alkaline conditions (the Hofer–Moest reaction, where alcohol production is the major process), there is little experimental evidence to suggest appreciable further oxidation of such a primary radical to R^+. Where R· is secondary, tertiary, allylic, or benzylic, there is considerable evidence to suggest that further oxidation to R^+ is an important factor in at least some of the product formations (for an excellent summary of possible reaction paths, see ref. 4). Eberson (15, 16) and others (17, 18) have also shown that, under the usual Kolbe conditions, not only $RCOO^-$ and solvent but also un-ionized RCOOH and added substrate such as aromatic rings, as well as primary R·, can be oxidized easily to R^+. These latter processes do not always occur to a marked extent even though the experimentally applied voltage is sufficient. However, sometimes they can be important. For example, in the acetoxylation of aromatic substrates under Kolbe conditions (15, 17, 18), instead of a simple radical attack of CH_3COO· on ArH, the reaction involves a two-electron transfer from ArH to the anode, giving ArH^{2+}, which reacts with acetate ion to give $ArOCOCH_3$ and H^+.

In the present work involving electrolysis of *o*-halogenophenyl-substituted acids, the products are those that have been explained traditionally by free-radical intermediates, e.g. $Ar(CH_2)_nCOO$· attack on methanol to give methyl esters, and, by decarboxylation, production of $Ar(CH_2)_{n-1}CH_2$·, which reacts with an identical species to give dimer, with methanol to give monomeric hydrocarbon[1] by hydrogen abstraction, and with CH_3O·, from the oxidation of methanol, to give methyl ether. For the acids other than the substituted phenylacetic acids, there is no evidence to suspect any major involvement of carbonium ions, although they cannot be ruled out completely. We could postulate ether formation by $Ar(CH_2)_{n-1}CH_2^+$ attack on methanol, or tetralin formation by cyclization of $Ar(CH_2)_{n-1}CH_2^+$, but this would involve oxidation of primary radicals to carbonium ions. The reactions are more probably radical combination of $Ar(CH_2)_{n-1}CH_2$· and CH_3O·, and radical cyclization of $Ar(CH_2)_{n-1}CH_2$· to give the substituted tetralin. Bunyan and Hey (1) found that unsubstituted 5-phenylpentanoic acid, on electrolysis, gave small amounts (3.8–4.5%) of tetralin, and postulated radical cyclization in its production. We isolated similar low yields (3.5–7.0%) of the corresponding 5-halogenotetralins.

The formation of alcohols was small, which is in accord with past work. In an acid medium, alcohol formation is rarely pronounced and appears to come from reaction with the small amounts of water, either present in the methanol solvent or else often added to decrease cell resistance and improve current flow. Aldehyde products have only been important when aryl-substituted acetic acids were used; this was explained (19) on the basis of peroxide formation from the more stable benzyl-type radicals produced. *o*-Bromo- and *o*-chloro-phenylacetic acids both gave aldehyde products in a low yield (only a trace from *o*-chlorophenylacetic acid), and no aldehydes were detected in any of the other reactions.

The electrolysis products from the *o*-halogenophenylacetic acids were similar to those

[1]*Commonly used to describe this by-product and used here to indicate the character of the side chain even though a halogen substituent is present on the ring.*

from the longer chain acids and can be explained by purely radical processes. However, electrolytically generated benzyl radicals appear to be oxidized to carbonium ions with great ease; hence, carbonium ion intermediates should not be ruled out, especially in ether formation. It should be noted that we did not isolate, as have other workers with substituted phenylacetic acids, products which clearly are not derived from radical processes.

In all of our electrolyses, ester formation was small; although control reactions indicate ester formation to be minor in the absence of the passage of current, it could possibly take place by attraction of the un-ionized acid to the anode and reaction there with methanol. Other workers (1, 2) have encountered polymer formation during electrolysis, although our yields of polymer were never as high as have been reported (up to 90%). Polymer formation seems to occur readily when phenyl substitution is present. Our results and those of other workers could possibly involve oxidation of the aromatic ring, leading to high-boiling, polymeric products. This is only speculation, however, and further comment must await a more detailed analysis of the polymeric fractions obtained. No other products were isolated where oxidation of the aromatic ring was involved.

Two conclusions regarding the effect of the *o*-halogen substituent on electrolysis reactions of phenyl-substituted acids can be made. First, the halogen substituent is perfectly stable during electrolysis; no products, even in trace amounts, were found in which either chlorine or bromine was displaced from the aromatic ring. Even in the case of the substituted pentanoic acids, where internal cyclization of the alkyl radical occurs to give small yields of tetralins, it was always hydrogen which was displaced, never halogen. This stability is not surprising, but it is the first time it has been demonstrated by experimental work. Secondly, there is a more-uniform spread of yields among all of the normal by-products than other workers have usually found during Kolbe-type electrolyses, where often only one by-product (usually the ester) predominates. This spread of products is possibly due to the increase in the molecular weight of the acids used when a halogen substituent is present. The acid therefore moves through the solution to the electrodes more slowly and the electrolysis is less efficient. The solvent carries more than its normal share of the current. Methoxy radical concentration, and hence ether formation, increases. Also, a decrease in the alkyl radical concentration at the electrode occurs and attack on the solvent takes place more readily, with a resultant decrease in dimer formation. However, with the *o*-halogenophenylacetic acids, the stability of the benzyl-type radical or carbonium ion may be a more important factor in determining the products.

The work described herein represents the first detailed study of the electrolyses of a series of *o*-halogenophenyl-substituted acids. The low yields and spread of products probably mean that the reactions should not be regarded as good synthetic ones for the production of the appropriate Kolbe dimers. In some individual cases, however, since other synthetic methods for these compounds do not exist presently, the reactions might be used conveniently for small-scale preparations.

EXPERIMENTAL

Physical constants and analytical data for new compounds are given in Table II. Melting points were determined on a Leitz hot stage and are corrected; boiling points are uncorrected. Analyses were performed by Schwarzkopf Mircoanalytical Laboratory, Woodside, New York. Infrared spectra were taken with Beckman IR-5 and IR-9 infrared spectrophotometers. An Aerograph Autoprep model 700 gas chromatograph was used with either a 10 or 20 ft × ⅜ inch column of 30% SE-30 silicone gum rubber on 60–80 mesh Chromosorb W; separated components were collected by means of the fraction collector, with external cooling.

TABLE II

Physical constants and analytical results of new compounds

Compound	Boiling point (°C)	n_D^{25} or melting point (°C)	Analytical results (%) C Calculated	C Found	H Calculated	H Found	Cl or Br Calculated	Cl or Br Found
Starting acids								
4-*o*-Bromophenylbutanoic acid		85–86	49.40	49.59	4.56	4.82	32.88	33.01
5-*o*-Bromophenylpentanoic acid		43–44	51.38	51.60	5.10	5.26	31.09	30.99
Reference compounds								
Methyl 5-*o*-chlorophenylpentanoate	104–108 at 0.2 mm	1.5249	63.57	63.81	6.67	6.87	15.64	15.12
4-*o*-Bromophenylbutan-1-ol	102–103 at 0.2 mm	1.5577	52.42	52.68	5.72	5.77	32.88	32.72
4-*o*-Bromophenylbutyl methyl ether	98–100 at 0.5 mm	1.5300	54.33	54.62	6.22	6.24	32.87	32.70
4-*o*-Chlorophenylbutyl methyl ether	85–86 at 0.5 mm	1.5112	66.49	66.21	7.61	7.34	17.85	17.58
Electrolysis products								
Methyl *o*-bromophenylacetate	73–75 at 0.2 mm	1.5465	47.18	47.03	3.96	3.69	34.89	34.31
Methyl 3-*o*-bromophenylpropanoate	90–95 at 0.3 mm	1.5408	49.40	49.74	4.56	4.45	32.88	32.38
Methyl 4-*o*-bromophenylbutanoate	92–94 at 0.2 mm	1.5345	51.38	51.93	5.09	5.15	31.08	30.90
Methyl 4-*o*-chlorophenylbutanoate	105–110 at 0.2 mm	1.5245	62.11	62.08	6.16	6.26	16.67	16.92
Methyl 5-*o*-bromophenylpentanoate		44–45	53.15	53.40	5.58	5.56	29.47	29.18
1,4-Di-(*o*-bromophenyl)-butane		68–69.5	52.20	52.54	4.38	4.52	43.42	43.21
1,6-Di-(*o*-bromophenyl)-hexane		31.5–32	54.56	54.53	5.08	5.11	40.36	40.16
1,6-Di-(*o*-chlorophenyl)-hexane	162–165 at 0.2 mm	1.5582	70.35	70.25	6.56	6.58	23.09	22.91
1,8-Di-(*o*-bromophenyl)-octane	190–192 at 0.3 mm	1.5690	56.62	56.60	5.70	5.76	37.68	37.57
1,8-Di-(*o*-chlorophenyl)-octane	170–175 at 0.15 mm	1.5512	71.64	71.77	7.21	7.22	21.15	20.98
2-*o*-Chlorophenylethyl methyl ether	47–49 at 0.3 mm	1.5185	63.64	63.42	6.49	6.58	20.78	20.90
3-*o*-Chlorophenylpropyl methyl ether	60–62 at 0.4 mm	1.5155	65.04	64.94	7.09	7.01	19.24	19.30

Syntheses of o-Halogenophenyl-Substituted Acids

o-Halogenophenyl-Substituted Acetic and Propanoic Acids

o-Bromo- and *o*-chloro-phenylacetic acids, prepared according to the procedure of Misra (7), had melting points of 104–105.5° and 94–95°, respectively. Misra found melting points of 104–105.5° and 93–94°. The malonate procedure (9, 10) gave 3-*o*-bromophenylpropanoic acid, m.p. 96–98° (lit. m.p. 97–98° (9)), and 3-*o*-chlorophenylpropanoic acid, m.p. 95–96.5° (lit. m.p. 95–96° (10)).

4-o-Bromophenylbutanoic Acid

3-*o*-Bromophenylpropyl bromide (94.0 g, 0.34 mole), prepared by the procedure of Beeby and Mann (20), was added to sodium cyanide (20.0 g, 0.40 mole) in 40 ml of hot water and 100 ml of ethanol over 30 min. The mixture was heated under reflux for 5 h, cooled, and filtered. Ethanol was distilled under vacuum, giving crude 4-*o*-bromophenylbutanonitrile, which was heated under reflux with a solution of equal volumes (80 ml each) of concentrated sulfuric acid, acetic acid, and water for 12 h, and set aside overnight. An oily layer separated after addition of 1 000 ml of water. This layer and two ethereal extracts of the aqueous layer were dried over magnesium sulfate. Distillation gave a colorless liquid, b.p. 124–130° at 1.5 mm, which solidified when allowed to stand. Purified 4-*o*-bromophenylbutanoic acid (67.2 g, 81%) was obtained by recrystallization from carbon tetrachloride (Table II).

4-o-Chlorophenylbutanoic Acid

By a reaction similar to that described above, 4-*o*-chlorophenylbutanoic acid, m.p. 92–93.5°, was obtained (lit. m.p. 94–95° (21)).

5-o-Bromophenylpentanoic Acid

The malonate procedure described in refs. 9 and 10 was used, although on a larger scale, and gave 146 g (72%) of diethyl 3-*o*-bromophenylpropylmalonate (b.p. 186–201° at 1.5 mm) from 190 g (0.68 mole) of 3-*o*-bromophenylpropyl bromide. Hydrolysis and decarboxylation of the crude malonic acid gave 5-*o*-bromophenylpentanoic acid, b.p. 146–162° at 1.0 mm, m.p. 40–42°. Recrystallization from carbon tetrachloride gave 74.6 g (61%) of pure acid (Table II).

5-o-Chlorophenylpentanoic Acid

In a similar manner, 3-*o*-chlorophenylpropyl bromide (200 g, 0.86 mole) gave diethyl 3-*o*-chlorophenylpropylmalonate (154 g, 58%), b.p. 185–190° at 1.5 mm. Hydrolysis and decarboxylation yielded 5-*o*-chlorophenylpentanoic acid, b.p. 155–160° at 0.6 mm, m.p. 43–46°. Recrystallization from carbon tetrachloride gave m.p. 45.5–46.5° (lit. m.p. 46°, b.p. 166–167° at 1.0 mm (12)) and a yield of 73.4 g (61%).

Syntheses of Authentic Reference Compounds

Esters of o-Halogenophenyl-Substituted Acids

Concentrated sulfuric acid (2 ml) was added cautiously to 1.5–2.0 g of the appropriate acid in 15 ml of methanol. Heating under reflux for 1 h and work-up in the usual manner gave the pure ester, on distillation, in yields of 85–90%. Esters of all the acids previously described were prepared. New compounds are listed in Table II.

4-o-Bromophenylbutan-1-ol

4-*o*-Bromophenylbutanoic acid (10 g, 0.041 mole) in 100 ml of anhydrous ether was added to a stirred suspension of lithium aluminium hydride (2.5 g) in 100 ml of anhydrous ether, maintaining gentle reflux. The reaction mixture was heated under reflux for 1 h. After removal of 100 ml of ether, the cooled reaction mixture was hydrolyzed with 20 ml of water, followed by 50 ml of 10% sulfuric acid. After filtration, the ethereal layer was separated, washed with 10% sodium carbonate solution and then water, and dried over magnesium sulfate. Distillation gave 7.79 g (83%) of pure 4-*o*-bromophenylbutan-1-ol (Table II).

4-o-Chlorophenylbutan-1-ol

Preparation from 4-*o*-chlorophenylbutanoic acid, as described above, gave a colorless liquid, b.p. 113–115° at 0.9 mm, n_D^{25} 1.5351 (lit. b.p. 150–151° at 12 mm (22) and b.p. 97–98° at 0.7 mm (23)).

3-o-Bromophenylpropyl Methyl Ether and 3-o-Chlorophenylpropyl Methyl Ether

The 3-*o*-halophenylpropyl bromides were methylated with sodium methoxide (20). The resulting bromoether had b.p. 68–71° at 0.5 mm, n_D^{25} 1.5334 (lit. b.p. 127–129° at 15 mm (20)), and the chloroether is described in Table II.

4-o-Bromophenylbutyl Methyl Ether

4-*o*-Bromophenylbutan-1-ol (3.0 g, 0.0014 mole) was dissolved in methyl iodide (20 ml) and stirred with silver oxide (6.0 g) and anhydrous calcium sulfate (10 g) for 24 h. The crude product was chromatographed on silicic acid (2.5 × 20 cm), with benzene as eluent. Evaporation of the first 50 ml of eluent left a colorless liquid, which was distilled to give 1.23 g (36%) of the pure ether (Table II).

4-o-Chlorophenylbutyl Methyl Ether

4-*o*-Chlorophenylbutan-1-ol was methylated as described immediately above. Similar purification gave the ether (Table II).

Electrolysis of o-Halogenophenyl-Substituted Acids

General Method of Electrolysis

The cell used was fully described previously (6). The acid was dissolved in methanol, along with enough sodium to produce 5% neutralization. By using a D.C. supply of 50–80 V, 0.5–1.0 A was passed for about

3 times the theoretical. The temperature was kept below 40°. During the electrolysis, insoluble, apparently polymeric material deposited on the anode, causing the current to fall below the stated minimum periodically. The current was stopped, the anode deposit removed, and the reaction started again.

Isolation of products into acidic and neutral fractions was carried out as described before (6), except that continuous ether extraction for 24 h gave the neutral component. Negligible starting material was usually returned. The neutral fraction was distilled under vacuum, giving four to five major fractions plus a non-distillable, tarry residue.

Isolation and Identification of Products

Two general procedures were used to purify the crude distillation fractions from above. Gas–liquid chromatography (g.l.c.) indicated that the substituted acetic and propanoic acid products were fairly well separated by the first distillation. The first three fractions were redistilled and the fourth recrystallized or treated to column chromatography. The *o*-bromophenylacetic acid reaction is described in detail as representative, and others similar to it in only enough detail to show some physical constants and important variations. The substituted butanoic and pentanoic acid products were not well separated by the first distillation, and chromatography was necessary, both column and g.l.c. with fraction collection. The 4-*o*-bromophenylbutanoic acid reaction is representative, and other similar ones are only briefly described. Percentage yields are found in Table I. In some cases, the yields were estimated from the relative peak areas of the g.l.c. chromatograms, but wherever possible, the actual weights of pure collected fractions were used.

The products were identified by matching g.l.c. behavior, physical constants, and infrared spectra with those of authentic samples as well as literature values. The infrared spectra were as expected and are not described. New compounds were submitted for elemental analysis (see Table II for analysis figures and physical constants). As an additional confirmation of the identity of the esters, small-scale hydrolysis to the free acids and mixed melting points were used.

Electrolysis of o-Halogenophenyl-Substituted Acetic and Propanoic Acids

Electrolysis of *o*-bromophenylacetic acid (20.0 g, 0.093 mole) in 150 ml methanol yielded four initial distillation fractions: 1, 1.46 g, b.p. 40–59° at 0.35 mm; 2, 1.34 g, b.p. 60–85° at 0.35 mm; 3, 1.05 g, b.p. 95–115° at 0.35 mm; 4, 0.55 g, b.p. 125–135° at 0.35 mm. The tarry residue weighed 3.95 g, and 4.13 g (22%) of starting acid was returned. Polymeric material (2.35 g) deposited on the anode during the reaction. Fraction 1 was a mixture of *o*-bromobenzaldehyde (1.06 g) and methyl *o*-bromobenzyl ether (0.40 g), as estimated by g.l.c. Redistillation of *o*-bromobenzaldehyde gave b.p. 49–50° at 0.2 mm, n_D^{25} 1.5931 (lit. b.p. 118–119° at 12 mm, m.p. 22° (24)). Gas–liquid chromatography indicated that fraction 2 was methyl *o*-bromobenzyl ether containing some ester. After the ester was removed by basic hydrolysis, the ether was redistilled, b.p. 65–66° at 0.2 mm, n_D^{25} 1.5505, 1.08 g (lit. b.p. 106–107° at 16 mm (25)). Fraction 3 was mainly methyl *o*-bromophenylacetate, and redistillation gave 0.98 g. Fraction 4 was passed through a silicic acid chromatography column (20 × 2.5 cm). Elution with 1:1 *n*-hexane–benzene gave 2,2′-dibromodibenzyl (0.42 g), which, on recrystallization from methanol, had m.p. 84–84.5° (lit. m.p. 84.5° (20)).

The electrolyses of *o*-chlorophenylacetic, 3-*o*-bromophenylpropanoic, and 3-*o*-chlorophenylpropanoic acids were similar. The following variations in procedure or in physical constants are noteworthy: 2-*o*-bromophenylethyl methyl ether had n_D^{25} 1.5429 (no literature value) and 1,4-di-*o*-(bromophenyl)-butane was chromatographed on neutral alumina with elution by hexane; methyl 3-*o*-chlorophenylpropanoate had b.p. 65–66° at 0.3 mm, n_D^{25} 1.5170 (lit. b.p. 255° (26)), and no column chromatography was necessary, only recrystallization, to give 1,4-di-(*o*-chlorophenyl)-butane, m.p. 53.5–54° (lit. m.p. 51–52° (27)).

Electrolysis of o-Halogenophenyl-Substituted Butanoic and Pentanoic Acids

Electrolysis of 4-*o*-bromophenylbutanoic acid (15.0 g, 0.062 mole) in 130 ml methanol yielded four initial distillation fractions: 1, 2.43 g, b.p. 40–80° at 0.4 mm; 2, 1.83 g, b.p. 70–98° at 0.3 mm; 3, 1.84 g, b.p. 106–135° at 0.3 mm; 4, 1.92 g, b.p. 186–200° at 0.3 mm. The tarry residue weighed 1.71 g to go with 2.35 g deposited during electrolysis. Fraction 1 was chromatographed on the alumina column previously described, and eluted with hexane to give *o*-bromo-*n*-propylbenzene, 0.95 g, b.p. 51–52° at 0.7 mm, n_D^{25} 1.5405 (lit. b.p. 217–220°, n_D^{25} 1.5395 (28)), as well as 1.38 g of a yellow liquid, which appeared to be identical (by g.l.c.) with fraction 2 and was added to it. Fraction 2, now 3.22 g, was separated by g.l.c. with temperature programming from 200 to 300° on the 10 ft column; the yields were estimated from the chromatogram. *o*-Bromo-*n*-propylbenzene (0.35 g), 3-*o*-bromophenylpropyl methyl ether (1.33 g), 3-bromophenylpropan-1-ol (0.17 g), and methyl 4-*o*-bromophenylbutanoate (0.74 g) plus an unidentified component (0.71 g) were obtained. Fraction 3 was redistilled, giving 1.56 g of methyl 4-*o*-bromophenylbutanoate. Fraction 4, on recrystallization from methanol, gave 1.72 g of 1,6-di-(*o*-bromophenyl)-hexane.

The electrolyses of 4-*o*-chlorophenylbutanoic, 5-*o*-bromophenylpentanoic, and 5-*o*-chlorophenylpentanoic acids were similar, but, for the latter two acids, the g.l.c. separations were carried out on the 20 ft column at 250–320° and 200–300°, respectively. Significant variations in physical constants were: *o*-chloro-*n*-propylbenzene, b.p. 33–35° at 0.5 mm, n_D^{25} 1.5130 (lit. b.p. 79° at 10 mm, n_D^{16} 1.5213 (29)), and *o*-chloro-*n*-butylbenzene, b.p. 38–40° at 0.3 mm, n_D^{25} 1.5117 (lit. b.p. 53–54° at 2 mm, n_D^{25} 1.5087 (30)).

ACKNOWLEDGMENTS

The authors are indebted to the National Research Council of Canada for financial support.

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