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# Free Radical Reactions in Organic Electrode Processes. II. The Anodic Aroyloxylation of Anisole*

By Kikuhiko KOYAMA, Kunihisa YOSHIDA and Shigeru TSUTSUMI

*Department of Chemical Technology, Faculty of Engineering, Osaka University, Miyakojima-ku, Osaka*

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Electrolyses of an acetonitrile solution of benzoic acid containing triethylamine have been carried out in the presence of anisole by the use of a platinum anode in an undivided cylindrical glass cell under various conditions. The electrolysis with benzoic acid at 15—23°C gave *o*- and *p*-methoxyphenyl benzoates (60%) as the main products, but the *m*-isomer could not be detected. The ratio of the isomers was 2 (*ortho*) : 1 (*para*). The other products identified in this experiment were carbon dioxide and biphenyl. The yield of the benzoates decreased when the electrolysis temperature was raised. The peaks of carbon dioxide and biphenyl on the vapor phase chromatograms in the experiment at 84°C, on the contrary, were relatively large compared with that observed in the low temperature electrolysis. Analogous products were obtained from the electrolysis of both *p*-toluic and *p*-anisic acids. These results have been compared with those obtained from the thermal decomposition of diaroyl peroxide in anisole. The mechanism of this anodic aroyloxylation of anisole has also been discussed.

It has been widely accepted that the anodic oxidation of carboxylate anions, generally known as the Kolbe electrolysis, proceeds via the direct formation of free radicals by the discharge of the carboxylate anions:[1,2]

$$\mathrm{RCOO^-} \rightarrow \mathrm{RCOO\cdot} + \mathrm{e} \qquad (1)$$

$$\mathrm{RCOO\cdot} \rightarrow \mathrm{R\cdot} + \mathrm{CO_2} \qquad (2)$$

$$2\mathrm{R\cdot} \rightarrow \mathrm{R{-}R} \qquad (3)$$

As a characteristic reaction of free radicals, the above sequence involves only the radical decomposition (Eq. 2) and the coupling reaction (Eq. 3). One might, however, expect that, when suitable conditions are employed, these intermediate radicals would react through the more varied processes observed in the other free radical reactions.[3] Indeed, this expectation has been partially realized in some studies.

It has already been suggested that the formation of some non-dimeric hydrocarbons could arise from either disproportionation or hydrogen abstraction from a solvent.[4] Evidence that the electrolysis of some carboxylates affords products which might be formed through a rearrangement of intermediate radicals has been provided by several groups of workers.[5,6]

Recently, Corey and his co-workers[7] have shown that electrolytically-generated aliphatic radicals readily undergo further oxidation to carbonium

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* Presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

1) M. J. Allen, "Organic Electrode Processes," Reinhold Publishing Corporation, New York (1958), p. 97.

2) B. C. L. Weedon, "Advances in Organic Chemistry," Vol. 1, Interscience Publishers, Inc., New York (1960), p. 3.

3) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York (1957), p. 31.

4) Ref. 3, p. 581.

5) Breederveld and Kooyman, *Rec. Trav. chim.*, **76**, 297 (1957).

6) P. J. Bunyan and D. H. Hey, *J. Chem. Soc.*, **1962**, 324.

7) E. J. Corey and R. R. Sauers, *J. Am. Chem. Soc.*, **81**, 1743 (1959); E. J. Corey, N. L. Bauld, R. T. La Londe, J. Casanova, Jr. and E. T. Kaiser, ibid., **82**, 2645 (1960).

TABLE I. ELECTROLYSES OF *p*-SUBSTITUTED BENZOIC ACIDS (0.075 mol.) IN THE PRESENCE OF ANISOLE (0.46 mol.)

Solvent: Acetonitrile (30 ml.)[a]
Electrodes: Pt-Foils (3×2 cm.; gap, about 5 mm.)

| Substituent at *p*-position | Electrolysis-conditions | | | | Acid not recovered mol. | Products | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Temp. °C | Current amp. | Voltage V. | Time hr. | | Methoxyphenyl esters | | Biphenyls | Polymeric residue g. | Gases | |
| | | | | | | Yield % | Ratio *o*-/*p*- | | | $H_2$ | $CO_2$ |
| H | 15—23 | 0.33—0.05 | 83—100 | 41.5 | 0.072 | 60 | 2/1 | T** | 13.2 | M* | T |
| H | 84 | 0.3—0.08 | 55—98 | 59 | 0.049 | 42 | 2/1 | T | | M | T |
| $CH_3$ | 12 | 0.1—0.03 | 90—100 | 245 | 0.07 | 52 | 3/2 | | 12.7 | M | T |
| $CH_3$ | 10 | 0.1 | 50—99 | 66 | 0.055 | 34.7 | 3/2 | | | M | T |
| $CH_3O$ | 8—12 | 0.1 | 40—95 | 100 | 0.054 | 13.5 | 3/2 | | | M | T |

a) Triethylamine (1.5 ml.) was added into the solvent, except for the experiment with *p*-anisic acid. In the case of *p*-anisic acid, 4 ml. of triethylamine was used.

* M: major ** T: trace

ions, which then attack the solvent.

In addition to the findings described above, the free radicals produced in the Kolbe electrolysis are capable of attacking organic substrates, giving rise to either an addition to double bonds or a substitution on aromatic nuclei. Interesting attempts to use the Kolbe electrolysis as a source of free radicals for the additive dimerization of dienes and for the polymerization of vinyl monomers have been made by many investigators.[8-11] The anodic acetoxylation and methylation of aromatic compounds, which takes place when acetate anions are subjected to electrolysis in the presence of the aromatic compounds, have previously been reported,[12-14] even though further attention has not yet been devoted to these substitutions.

On the other hand, analogous aromatic substitutions occur during the course of the decomposition of diacyl peroxides in aromatic solvents, the thermal decomposition of some lead tetracarboxylates in aromatic compounds, and the reaction of the complexes formed from a dry silver salt of a carboxylic acid and a halogen, with aromatic compounds, and it is well recognized that these compounds could readily undergo breakdown into acyloxy and hydrocarbon radicals, which then participate in aromatic substitutions.[15]

It thus becomes desirable to compare the products of the Kolbe electrolysis, which was carried out in the presence of an aromatic compound, with those of the decomposition of the corresponding diacyl peroxides in the aromatic solvent; we can thus extend our knowledge of the characteristics of the electrochemically-generated free radicals.

The present investigation will deal with the electrolysis of a salt of some aromatic acids in the presence of anisole, not merely because of the high availability of data on the decomposition of dibenzoyl peroxide in anisole, but also because of the paucity of information on the electrochemical behavior of aromatic acids.

## Results and Discussion

The electrolyses which will now be reported on were carried out under various conditions in a mixture of anisole and acetonitrile containing triethylamine. Two platinum foil electrodes were used; a detailed description of the apparatus was given in a previous paper.[13]

In all cases, the mixtures became brownish, and a sticky non-conducting polymer was frequently deposited on the anode. The current, therefore, was gradually decreased until the end of the electrolysis.

The gaseous products evolved during these electrolyses were analyzed by vapor-phase chromatography, while the liquid products were generally treated as will be described below. After the electrolyzed mixtures were worked up to remove the solvents and recover the acids, the oils remaining were distilled under reduced pressure, and the distillates were chromatographed on alumina and/or treated with alcoholic potassium hydroxide. Qualitative and quantitative determinations of phenolic isomers and neutral fractions obtained from the hydrolysis products were carried out by vapor-phase chromatography, and the acidic fractions were characterized by mixed-melting-point measurements. The crystals isolated by column chromatography were identified as the esters

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8) R. V. Lindsey, Jr., and M. L. Peterson, ibid., **78**, 2073 (1956).

9) W. Smith and H. G. Gilde, ibid., **81**, 5325 (1959).

10) W. Smith and H. G. Gilde, ibid., **82**, 659 (1960).

11) S. Goldschmidt and E. Stöckl, *Chem. Ber.*, **85**, 630 (1952).

12) C. L. Wilson and T. Hayashi, Abstracts of papers presented at the 126th Meeting of the American Chemical Society, New York, N. Y., 1954, p. 78—O.

13) K. Koyama, Y. Odaira and S. Tsutsumi, *Technol. Repts. Osaka Univ.*, **12**, 463 (1962).

14) L. F. Fieser, R. C. Clapp and W. H. Daudt, *J. Am. Chem. Soc.*, **64**, 2052 (1942).

15) G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, Oxford (1960), pp. 41—42.

themselves by the usual methods.

The results obtained with benzoic, *p*-toluic and *p*-anisic acids are summarized in Table I. Percentage yields, based on the amount of the acid not recovered at the end of the electrolysis, are given for those products which were isolated quantitatively.

As has been indicated above (Table I), the major products in each experiment were *o*- and *p*-methoxyphenol esters of the corresponding aromatic acids; no *m*-isomers could be detected. The proportions of the isomers were nearly 2(*ortho*) to 1(*para*) with benzoic acid, and 3(*ortho*) to 2(*para*) with *p*-toluic and *p*-anisic acids.

From the results of the experiment with benzoic acid, it is evident that the extent of such anodic benzoyloxylation decreases when the temperature is raised to 84°C even though the value for the isomer distribution still remains constant. It might be expected that benzene, biphenyl, methoxybiphenyls and/or phenyl benzoate would be formed, either by the attack of phenyl radicals on the anisole or by the radical-recombination reaction. There was, however, no evidence for the presence of these products, except for the biphenyl, in our present studies with benzoic acid. In addition to the above observations, the formation of 1, 2-diphenoxyethane and phenoxymethylanisoles could not be observed in these electrolyses.

The gases evolved from these electrolyses consisted of hydrogen, accompanied by a trace of carbon dioxide.

The peak of carbon dioxide on the vapor phase chromatogram in the experiment with benzoic acid at 84°C, was relatively large compared with that observed in low temperature electrolysis.

The results thus obtained indicate that the high temperature electrolysis led to the decomposition of benzoyloxy radicals into carbon dioxide and phenyl radicals, which subsequently dimerized to give biphenyl as a normal Kolbe product.

In all cases, a considerable amount of polymeric residues was obtained. Although further treatment of the residues was unsuccessful because of their low solubility in usual organic solvents, their infrared spectra indicated the presence of both methoxyl and phenyl groups.

Results similar to those with benzoic acid were obtained in the experiments with *p*-toluic and *p*-anisic acids, except that both the yield of the esters and the value for the isomer distribution slightly varied. However, the differences in the isomer distribution are insignificant since the figures based on the peak area on the vapor-phase chromatograms admit some allowances in their calculations.

The results described herein exhibit a striking contrast to those obtained from the decomposition of dibenzoyl peroxide in anisole.[16-19] It may be suggested, in principle, that the radicals from dibenzoyl peroxide, both benzoyloxy and phenyl radicals, attack the aromatic substrates, giving rise to either the benzoyloxylation or the phenylation of aromatic nuclei. Both reactions, as a matter of course, have been observed in the homolytic aromatic substitutions. However, the extent of benzoyloxylation is generally small, especially with simple and monosubstituted aromatic compounds, since benzoyloxy radicals appear to be considerably less reactive entities than phenyl radicals in aromatic substitution.

Recently, Lynch and Moore[19] have found that the homolytic benzoyloxylation of anisole with dibenzoyl peroxide, which had been neglected in previous works, occurred to an appreciable extent at 80°C, even though phenylation still proceeded as the main reaction.

The predominance of benzoyloxylation over the phenylation in our experiment clearly indicates the characteristics of the anodically-generated benzoyloxy radical. An explanation for such an anomalous stability of benzoyloxy radicals is provided by the facts that this radical is generated at the anode, at a comparatively low temperature, and that biphenyl is only product which was formed with phenyl radicals by their coupling reaction. These facts imply that the anodically-produced benzoyloxy radicals are stabilized and suppressed to undergo their rapid decarboxylation by adsorption on the electrode surface, and that their subsequent reactions take place only on the electrode surface.

If free benzoyloxy radicals existed in a bulk solution during these electrolyses, a considerable amount of methoxybiphenyls would be produced through the spontaneous decomposition of the benzoyloxy radicals.

Furthermore, it may be assumed that the formation of biphenyl arose from the coupling of the phenyl radicals which were adsorbed on the electrode or which existed in the original solvent cage, since it seems that biphenyl and phenyl benzoate are formed by the "cage" recombination reaction of the radicals generated by the decomposition of dibenzoyl peroxides.[20]

The question may be raised, then, of how such stabilized benzoyloxy radicals react with anisole to afford methoxyphenyl benzoates. The recent work by Zweig et al.[21] has indicated that anisole can also be polarographically oxidized, with the

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[16] T. Suehiro, *J. Chem. Soc. Japan*, *Pure Chem. Sect.*, (*Nippon Kagaku Zassi*), **72**, 301 (1951).

[17] C. S. Rondestvedt and H. S. Blanchard, *J. Org. Chem.*, **21**, 229 (1956).

[18] D. R. Augood and G. H. Williams, *Chem. Revs.*, **57**, 123 (1957).

[19] B. M. Lynch and R. B. Moore, *Canadian J. Chem.*, **40**, 1461 (1962).

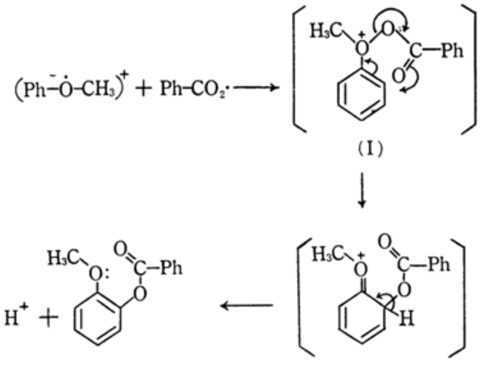
[20] C. G. Swain, L. J. Schaad and A. J. Kresge, *J. Am. Chem. Soc.*, **80**, 5313 (1958).

[21] A. Zweig, W. G. Hodgson and W. H. Jura, ibid., **86**, 4124 (1964).

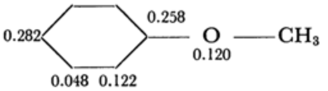
values of +1.76 V. (vs. SCE) and 19.4 μamp./mmole for the half-wave potential and the diffusion current respectively, to produce its cation radical in acetonitrile. Their finding will help provide an explanation of this question. It may suggest that the occurrence of the simultaneous oxidation of anisole molecules with benzoate anions would result in the facile attack of adsorbed benzoyloxy radicals on anisole cation radicals, which are produced by the loss of an electron from anisole at the anode, leading to the predominant formation of methoxyphenyl benzoates.

There is, as yet, an unsolved problem concerning the isomer distribution. The observed isomer distribution in this reaction is analogous to those in the anodic acetoxylation of anisole[12] and the benzoyloxylation with dibenzoyl peroxide,[19] in which no *m*-isomer could be detected and *ortho-para* orientation has been observed to be preferred. The predominance of *o*- and *p*- positions in this anodic substitution appears to be partly due to the polar character of the benzoyloxy radicals. The benzoyloxy radical, that is, seems to be an electrophilic species, it may thus be expected to attack preferentially the points of high electron density in the anisole.

However, a more satisfactory explanation for the orientation in this substitution will be given by the assumption that the coupling reaction of a benzoyloxy radical with an anisole cation radical will occur at the positions of high spin density in the cation radical. Lynch and Moore have already proposed the analogous coupling for the ortho benzoyloxylation of anisole with dibenzoyl peroxide[19]; i. e.:



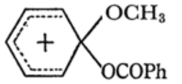
Furthermore, Zweig's calculation[21] of the spin densities for the ring and oxygen positions of the anisole cation radical affords abundant evidence in support of our assumption. The values of the spin density for each position are shown in Fig. 1.



$$\left[\begin{array}{l}\alpha_O=\alpha_C+2.0\beta_{CC}\\ \beta_{CO}=0.8\beta_{CC}\end{array}\right]$$

Fig. 1. The spin densities of the anisole cation radical.[21]

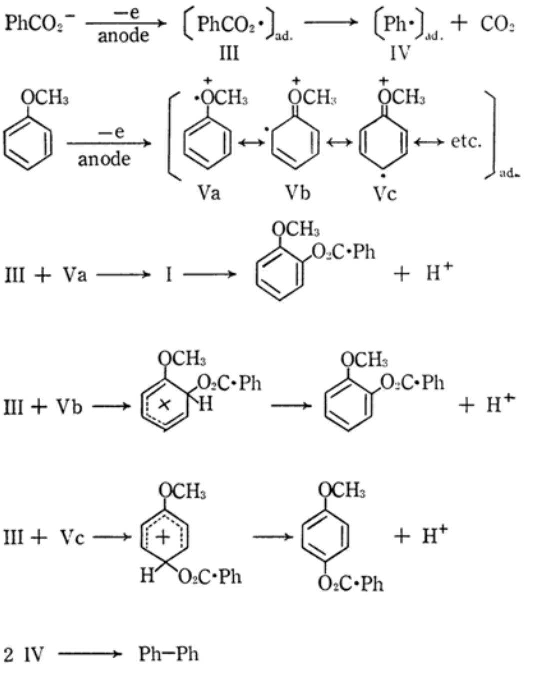
Although a high spin density on the substituted carbon atom in the benzene ring appears in their calculation, the possibility of the coupling at this position is very small because of the unfavorable steric requirement of this coupling or because of the low stability of a σ-complex (II) if one is formed in the transition state for this reaction.



(II)

Accordingly, *o*- and *p*-methoxyphenyl benzoates would be formed by either process, a direct attack of benzoate radicals on *o*- and *p*-positions of the cation radical or a cyclic rearrangement of the indirect coupling intermediate (I), as has been suggested by Lynch et al.

On the basis of the argument described above, the most probable scheme for this anodic aromatic substitution may be shown thus:



However, another mechanism, one involving the reaction of a benzoate anion with an anisole cation radical generated at the anode, might also be suggested for the formation of methoxyphenyl benzoates.

## Experimental

All the melting points and boiling points described here are uncorrected. The infrared spectra were obtained with a Simadzu infrared spectrophotometer IR-27B. A Shimadzu gas chromatograph GC-2A, equipped with a 3 m., 4 mm. copper column packed with 25% Silicone DC-550 on Shimalite (Chromosorb P) was employed for the analysis of the phenolic and neutral fractions; it was operated at 180°C, using hydrogen as a carrier gas. A vapor-phase chromatogram of the gaseous products was also obtained on the same instrument equipped with a 0.5 m., 4 mm. silica gel column, which was operated at 13°C. The carrier gas was nitrogen.

Electrolyses were carried out in a cylindrical cell fitted with a condenser; two platinum foil electrodes (3×2 cm.; gap about 5 mm.) were also used. During the electrolyses, the cell was cooled in a bath of cold water containing ice to control the temperature, and the contents were stirred magnetically.

**Materials.**—Commercially-available aetonitrile was dried over anhydrous magnesium sulfate and distilled (b. p. 81°C). Triethylamine was dried over potassium hydroxide and distilled. Anisole was washed with a 10% aqueous sodium hydroxide soultion and then with water, dried over calcium chloride, and distilled before use (b. p. 155°C). Benzoic, *p*-toluic and *p*-anisic acids were obtained commercially and used without further purification.

**The Electrolysis of the Ammonium Salt of Benzoic Acid in the Presence of Anisole.**—A solution of benzoic acid (9.2 g., 0.075 mol.) and anisole (50 ml., 0.46 mol.) in acetonitrile (30 ml.) containing triethylamine (1.5 ml.) was electrolyzed at 15—23°C, with an applied potential of 83—100V. for 41.5 hr. at a current of 0.33—0.05 amp.; the solution thus became slightly alkaline. The current was gradually decreased from 0.33 to 0.05 amp.; 0.47 faraday had been passed through the solution by the end of the electrolysis.

The acetonitrile was removed from the electrolyzed solution under reduced pressure, and the residue was dissolved in ether. The ethereal solution was then extracted with a saturated aqueous sodium hydrogen carbonate solution, washed with 10% hydrochloric acid and then with water, dried over anhydrous magnesium sulfate, filtered, and evaporated to yield 54.3 g. of a brownish residual oil.

When the aqueous solution was acidified with 10% hydrochloric acid, 0.3 g. of the unchanged benzoic acid was recovered. The residual oil, distilled under reduced pressure, gave the following fractions:

Fraction I: b. p. 58°C/15 mmHg, 30.8 g.
Fraction II: b. p. 148—154°C/2.5 mmHg, 10.3 g.
Residue: 10.2 g.

Fraction I consisted of anisole, which was identified by vapor-phase chromatography.

The infrared spectrum of Fraction II indicated the presence of benzoates. Thus, a portion (5 g.) of Fraction II was heated under reflux with 5% potassium hydroxide in ethanol for 16 hr. After the ethanol had been removed, the residue was acidified and extracted twice with ether. The combined extracts were worked up in the usual manner in order to separate them into acidic, phenolic and neutral fractions.

From the acidic fraction, 2.3 g. of the crude benzoic acid was obtained and recrystallized from benzene. The acid melted at 119.5—121°C (lit.[22] m. p. 122.4°C); the melting point was undepressed on admixture with an authentic sample. Moreover, the infrared spectrum of the acid (KBr disk) was essentially identical with that of authentic benzoic acid.

The phenolic fraction (2.4 g.) displayed two peaks with the same retention times as those of authentic *o*- and *p*-methoxyphenols on a vapor phase chromatogram; the ratio of the isomers was determined by an internal standard method to be 2 (*ortho*): 1(*para*). Moreover, the infrared spectrum of this fraction (liquid film) exhibited absorption bands at 733, 745, 825, 1022, 1037, 1105, 1150, 1175, 1220, 1260, 1300, 1380, 1440, 1450, 1510, 1600 and 3400 cm$^{-1}$. These absorption bands can easily be assigned to the *o*- and *p*-methoxyphenols respectively. If the phenolic fraction contained the *m*-isomer, it should show the additional absorption bands at 690, 770, 1160, 1200, 1290, 1500 and 1600 cm$^{-1}$ in its infrared spectrum.

The neutral fraction (0.2 g.) obtained from the hydrolysis product of Fraction II displayed three peaks on a vapor-phase chromatogram. One of them had the same retention time as biphenyl, but this peak was relatively small compared to the other ones. No further attempts were made to determine the products which correspond to the other peaks. It is, however, evident that 1, 2-diphenoxyethane, phenoxymethylanisoles and methoxybiphenyls were not major constituents of this fraction. The fraction, however, displayed major absorption peaks in the infrared spectrum at 700, 755, 1025, 1228, 1450, 1600, 2860 and 3200 cm$^{-1}$ (liquid film).

The remaining portion (5.3 g.) of Fraction II was chromatographed on alumina and eluted with benzene to afford two crude solids after the solvent had been removed. The solid rapidly eluted was recrystallized from ethanol and gave a white crystal (2.3 g.; m. p. 57—58°C, undepressed by admixture with *o*-methoxyphenyl benzoate prepared by an entirely different method). The infrared specturm (KBr disk) was essentially identical with that of an authentic sample.

Found: C, 73.63; H, 5.14. Calcd. for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30%.

The recrystallization of the slowly-eluted solid from ethanol gave a white crystal (1.5 g.), m. p. 87.5—88.1°C; the melting point of this crystal was not depressed on admixture with *p*-methoxyphenyl benzoate. The infrared spectrum (KBr disk) was identical with that of an authentic sample.

Found: C, 73.62; H, 5.64. Calcd. for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30%.

The brownish polymeric residue was insoluble in ether and ethanol, but slightly soluble in acetone and benzene. The infrared spectrum exhibited characteristic absorption bands which could be assigned to the methoxyl group and to the aromatic ring.

A vapor-phase chromatographic analysis indicated that the gaseous product consisted mainly of hydrogen, plus a trace of carbon dioxide.

**The Electrolysis of the Benzoate Anion in the Presence of Anisole at a High Temperature.**—The electrolysis was carried out at 84°C, with an applied potential of 55—98 V., at a current of 0.1—0.3 amp., for 59 hr. The results obtained from this electrolysis are summarized in Table I.

The peaks of carbon dioxide and biphenyl on the vapor-phase chromatograms were relatively large compared with those observed in a low-temperature electrolysis.

**The Electrolysis of the Triethylammonium Salt of *p*-Toluic Acid in the Presence of Anisole.**—A solution of *p*-toluic acid (10.2 g., 0.075 mol.) and

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[22] "The Merck Index" (seventh edition), Merck & Co., Inc., New Jersey (1960), p. 133.

anisole (50 ml., 0.46 mol.) in acetonitrile (30 ml.) containing triethylamine (1.5 ml.) was electrolyzed at 10°C, for 66 hr. A current of 0.1 amp. was maintained, while the voltage was varied from 50 to 99 V. By the end of electrolysis, about 0.25 faraday had been passed through the solution.

The procedure used for the isolation and the identification of the product was identical with that described in the experiment with benzoic acid.

After the work-up of the electrolyzed mixture, 2.6 g. of *p*-toluic acid was recovered. The distillation of the remaining oil under reduced pressure gave unreacted anisole (ca. 24.3 g.), a fraction (4.7 g.), b. p. 160—166°C/2.7 mmHg, and a residue.

The hydrolysis of 3.5 g. of the high-boiling fraction with 5% potassium hydroxide in ethanol for 20 hr. afforded an acid (1.7 g.), phenols (1.6 g.) and neutral substances (0.3 g.). The acid was characterized as *p*-toluic acid, m. p. 179—180.5°C, undepressed on admixture with an authentic sample. The infrared spectrum of the acid was identical with that of the authentic sample. The phenols were shown to be *o*- and *p*-methoxyphenols by vapor-phase chromatography; the ratio of these isomers was found to be 3 (*ortho*): 2 (*para*).

In addition, two crystals were isolated by chromatography; they were identified as *o*- and *p*-methoxyphenyl *p*-toluates.

The melting point of *o*-methoxyphenyl *p*-toluate was 75—76°C; infrared spectrum (KBr disk): 750, 835, 1020—1035 (2 bands), 1065, 1100, 1160, 1265, 1450, 1490, 1600 and 1710 cm$^{-1}$.

Found: C, 74.03; H, 5.91. Calcd. for $C_{15}H_{14}O_3$: C, 74.36; H, 5.83%.

The infrared spectrum of *p*-methoxyphenyl *p*-toluate, m. p. 95.5—96.5°C, exhibited characteristic bands at 835, 1025, 1035, 1065, 1100, 1165, 1200, 1265, 1450, 1500, 1600 and 1715 cm$^{-1}$ (KBr disk).

Found: C, 74.27; H, 6.08. Calcd. for $C_{15}H_{14}O_3$: C, 74.36; H, 5.83%.

**The Electrolysis of the Triethylammonium Salt of *p*-Anisic Acid in the Presence of Anisole.** —A solution of *p*-anisic acid (11.4 g., 0.075 mol.) and anisole (50 ml., 0.46 mol.) in acetonitrile (30 ml.) containing triethylamine (4 ml.) was electrolyzed at 8—12°C, for 100 hr. The current was maintained at 0.1 amp., while the voltage was increased from 40 to 95 V.

After the electrolysis, unchanged anisic acid (3.1 g.) was recovered. The residual oil was distilled under reduced pressure to give the following fractions:

Fraction I: b. p. 46°C/11 mmHg, 23.4 g.
Fraction II: b. p. 92—181°C/3 mmHg, 2.1 g.
Residue: 9.4 g.

Fraction I was shown by vapor-phase chromatography to consist of anisole. A portion (0.8 g.) of Fraction II was submitted to hydrolysis. An acidic fraction obtained from the hydrolysis product consisted of *p*-anisic acid (0.4 g.), m. p. and m. m. p. 184°C. The infrared spectrum was identical with that of an authentic sample.

The phenolic fraction (0.4 g.) was found to be a mixture of *o*- and *p*-methoxyphenols ( 3 : 2 ratio).

Seven peaks were indicated on the vapor-phase chromatogram of the neutral fraction (0.1 g.) separated from the hydrolysis product, but this fraction could not be further identifed.

**The Preparation of Authentic Samples.** — Methoxybiphenyls were prepared by Gomberg's method,[23] and *o*- and *p*-methoxyphenyl benzoates were prepared by the reaction of benzoyl chloride with the corresponding methoxyphenols. 1, 2-Diphenoxyethane was prepared according to the directions of Drahowzal et al.[24] The syntheses of authentic phenoxymethylanisoles were carried out by the method of Claisen.[25]

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[23] W. E. Bachmann and R. A. Hoffman, "Organic Reactions," Vol. 2, John Wiley & Sons, New York (1944), p. 224.

[24] F. Drahowzal and D. Klanann, *Chem. Abstr.*, **46**, 8036 (1952).

[25] L. Claisen, *Annal.*, **442**, 244 (1925).