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ELECTROLYTIC INTRODUCTION OF ALKYL GROUPS

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When a mixture of benzaldehyde and ethyl iodide, saturated with tetraethylammonium iodide, was electrolyzed, the ethyl ether of ethylphenyl carbinol, $C_6H_5CH:(C_2H_5)OC_2H_5$, was one of the products formed at the cathode. In addition to this ether, there were also formed at the cathode unsymmetrical diphenyl-ethylene glycol, hydrobenzoin (symmetrical diphenyl-ethylene glycol), stilbene (symmetrical diphenyl-ethylene), a gas which was apparently ethylene, a benzoate corresponding in odor and volatility to ethyl benzoate, an iodide similar to but not identical with benzyl iodide and a non-crystallizing residual tar.

Iodine was liberated at the anode when a platinum anode was used, while in the case of a copper or lead anode some iodine was formed together with cuprous or lead iodide. When the diaphragm separating the anode and cathode compartments was thick enough to prevent the diffusion of iodine, the quantity of iodine and iodide found in the anode compartment at the end of the electrolysis was that theoretically required by the quantity of electricity used.

Preliminary experiments, in which methyl iodide was used in the electrolysis instead of ethyl iodide, indicate that the reaction is similar in this case. A liquid was obtained which had an odor like that of the ethyl ether of ethylphenyl carbinol obtained by the use of ethyl iodide. This liquid, when oxidized, gave acetophenone and is therefore believed to be the corresponding methyl ether of methylphenyl carbinol.

Attempts to introduce methyl groups into benzonitrile, propionitrile and acetone by this method were unsuccessful. The formation of methane in practically theoretical current yield was the only tangible reaction occurring at the cathode during the electrolysis of mixtures of these substances with methyl iodide.

Discussion of Results

The conversion of benzaldehyde (I) into the ethyl ether of ethylphenyl carbinol (II), which has been carried out electrolytically, is analogous on the one hand to the formation of benzyl alcohol (III) by reduction of benzaldehyde, and on the other hand to the formation of ethylphenyl carbinol (IV) from benzaldehyde by means of the Grignard reaction.

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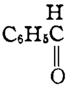
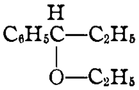
[1] The junior author held a Du Pont Fellowship for a part of the time during which this work was being carried on. He therefore wishes to express his thanks to E. I. Du Pont de Nemours and Co., for this assistance.



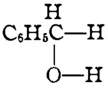
$C_6H_5\overset{H}{C}{=}O$

I



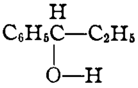
$C_6H_5\overset{H}{C}(-O-C_2H_5)-C_2H_5$

II



$C_6H_5\overset{H}{C}(-O-H)-H$

III



$C_6H_5\overset{H}{C}(-O-H)-C_2H_5$

IV

In all three reactions the entering groups become attached to the carbon and oxygen atoms of the carbonyl group of the benzaldehyde. Thus, by electrolyzing a mixture of benzaldehyde and ethyl iodide, two ethyl groups are introduced into these positions in the benzaldehyde molecule. By treating benzaldehyde with sodium amalgam[1a] or with hydrogen in the presence of platinum,[2] two hydrogen atoms are introduced into the benzaldehyde molecule in the same positions. By treating benzaldehyde with ethylmagnesium iodide[3] (formed from magnesium and ethyl iodide) an ethyl group is attached to the carbon atom of the carbonyl group in the formation of $C_6H\,CH{:}(C_2H_5)OMgI$. By decomposing this magnesium compound with water, ethylphenyl carbinol results, in which hydrogen is attached to the oxygen atom of the carbonyl group.

It will be seen that one of the ethyl groups which is introduced electrolytically into the benzaldehyde molecule with the formation of the ethyl ether of ethylphenyl carbinol enters at exactly the same point as does the ethyl group introduced by means of the Grignard reaction; that is, it becomes attached to the carbon atom of the carbonyl group. The electrolytic reaction is therefore very similar to the Grignard reaction, as regards both the nature of the products formed and the starting materials, which are benzaldehyde and ethyl iodide in both cases. In carrying out the Grignard reaction, however, metallic magnesium or some other strongly electropositive metal must be used together with the aldehyde and iodide. Now it is possible in many cases where metals are used as reducing agents for organic compounds, to carry out the same reduction without the use of active metals by placing the substance to be reduced at the cathode of a cell and passing a current of electricity through it. In the same way, by passing a current through a cell containing benzaldehyde and ethyl iodide at the cathode, a reaction very similar to the Grignard reaction has been brought about as described in this paper, without the use of magnesium or other active metal.

The electrolytic introduction of ethyl groups into benzaldehyde, besides bearing a formal resemblance to the reduction of benzaldehyde to benzyl alcohol, is also analogous to those reduction reactions which may be carried out electrolytically at the cathode of a cell, since the introduction of ethyl groups also takes place at the cathode. Indeed, if we define reduction as the addition of electrons, the formation of the ethyl ether of ethylphenyl

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[1a] Friedel, *Bull. soc. chim.*, **1862**, 18.

[2] Vavon, *Compt. rend.*, **154**, 359 (1912).

[3] Grignard, *Ann. Univ. Lyons*, **1901**, 1–116; *Chem. Centr.*, **1901**, II, 623.

carbinol from benzaldehyde might itself be classified as a reduction, since this transformation takes place at the cathode only during the passage of the current and therefore apparently requires electrons. According to this, the reaction is $C_6H_5CHO + 2C_2H_5I + 2e \longrightarrow C_6H_5CH{:}(C_2H_5)\text{-}OC_2H_5 + 2I^-$.

The electrolytic introduction of alkyl groups appears to take place with difficulty and other reduction reactions are brought about simultaneously by the passage of the current. Thus part of the benzaldehyde is reduced to the two diphenyl-ethylene glycols and to stilbene, the reaction involving the addition of hydrogen or the removal of oxygen, as is the case in most organic reductions. The formation of such reduction products instead of compounds containing alkyl groups is in agreement with the observation[4] that ethylmagnesium bromide under certain conditions may act as an ordinary reducing agent, with the formation of ethylene as a by-product. This view of the formation of hydrobenzoin, etc., by the electrolysis of the benzaldehyde solution is supported by evidence that ethylene is also formed at the same time. The formation of hydrobenzoin accordingly may take place as follows: $2C_6H_5CHO + 2C_2H_5I + 2e \longrightarrow C_6H_5CH(OH)\text{-}CH(OH)C_6H_5 + 2C_2H_4 + 2I^-$.

The failure to introduce alkyl groups into benzonitrile, propionitrile, and acetone electrolytically is not unexpected, in view of the difficulty of introducing alkyl groups into benzaldehyde by this method.

Experimental Work

The Apparatus.—The cell employed for most of the electrolyses consisted of an annular space 4 cm. wide, 18 cm. high and 16 cm. in outer diameter formed by a bottle A placed within a larger bottle B. See Fig. 1.

A crack just below the shoulder of the outer bottle allowed the removal of the upper part so that the inner bottle A and the electrodes could be introduced. The inner bottle A was held in place by a rod C fitted into the cork D in the mouth of the outer bottle. The cathode E, made of copper gauze or thin sheet copper, 900 sq. cm. in area, fitted against the inner wall of the outer bottle. The anode F of thick sheet copper or lead, 600 sq. cm. in area, was fitted around the outside of the inner bottle. The distance between the electrodes was 4 cm. and the capacity of the apparatus was about 1.5 liters.

An asbestos diaphragm G was placed between the electrodes so as to prevent the mixture of the solutions surrounding the anode and cathode. This diaphragm was made by moulding wet asbestos paper around the sides and bottom of a bottle of appropriate size, removing the bottle, and baking the asbestos shell in an oven at 120° for several days to drive off the water. The diaphragm was of such a size that the volume of the anolyte was about one-third that of the catholyte or cathode solution. A new diaphragm was used for each electrolysis.

Electrical connections with the electrodes were made through mercury cups H and I fitted into the cork D. Platinum wires sealed in these cups were connected to the electrodes by copper wires. The cork D also carried the funnel J, with a stop-

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[4] Hess and Rheinboldt, *Ber.*, **54**, 2043 (1921).

cock at the bottom as shown, for the introduction of material into the cell, and also a dropping funnel K, with the tip so bent that, by turning it, liquid could be delivered into either the cathode or the anode compartment.

In assembling the cell, the cathode E and the diaphragm G were first put in place in the large bottle B, then the cracked-off upper part of B, carrying the cork D with the inner bottle A and the anode F attached by the rod C, was lowered over the rest of the cell so that the cathode could be connected with its lead-wire. The two parts of the bottle B were then fitted together and cemented with glue. The joint was made gas-tight by wrapping with electrician's tape and coating with collodion.

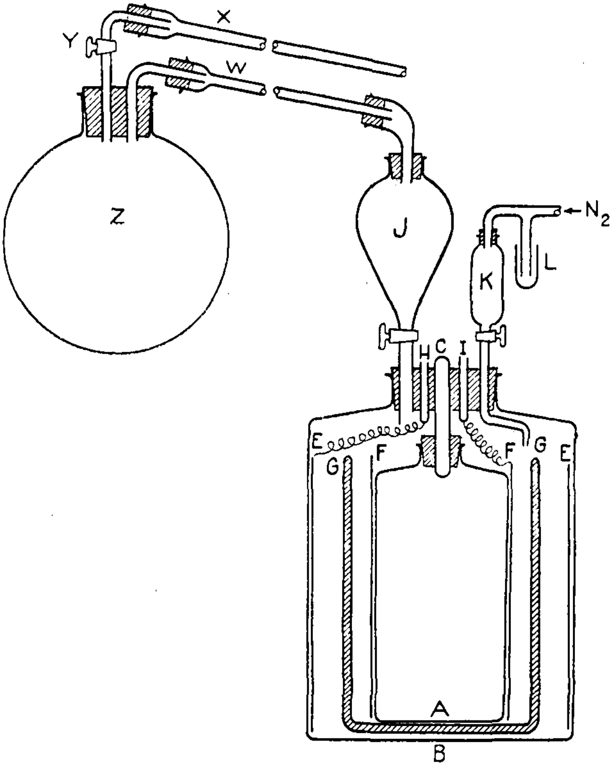

Fig. 1.

Filling the Cell for Electrolysis.—The cell was first filled with nitrogen by repeated evacuating and flooding with nitrogen which was dried by bubbling through concd. sulfuric acid. The stopcock at the bottom of the funnel J was closed during this operation and the gas was introduced through the dropping funnel K.

Two liters of benzaldehyde, purified as described below and containing some water from this treatment, was placed in the 3-liter, round-bottom flask Z as quickly as possible to avoid oxidation by the air. Dry nitrogen was then passed into the cell through the dropping-funnel K, out through the funnel J, through the condenser W into the flask Z which contained the benzaldehyde, and finally through the stopcock Y and out through the condenser X. This was continued until the percentage of oxygen in the gas issuing at the end of the condenser X, determined by absorption in alkaline pyrogallate solution, was the same as that in the nitrogen entering the apparatus (0.2%). The flask Z was then heated and a mixture of water and benzaldehyde was distilled over into the condenser X by passing a sufficiently rapid current of nitrogen through the condenser W into the flask which contained the benzaldehyde to prevent the passage of benzaldehyde vapor into W. When the water had thus been completely removed from the benzaldehyde in the flask, the stopcock Y was closed and the dry benzaldehyde was distilled through the condenser W into the funnel J and from there allowed to flow into the cell. The benzaldehyde first filled the anode compartment and slowly filtered through the diaphragm to the cathode side. The gas in the apparatus was kept at slightly more than atmospheric pressure during the distillation by causing nitrogen to bubble constantly through the trap L, a side tube dipping a short distance into a pool of mercury. In this way air was prevented from entering the apparatus through any possible leaks. The last portion of benzaldehyde was not distilled into the cell. When the distillation was finished, the stopcock at the bottom of the funnel J was closed and the cell was allowed to cool to room temperature, the pressure of nitrogen being always kept slightly greater than atmospheric.

These precautions were taken because it was thought essential to have no benzoic acid, which is rapidly formed from benzaldehyde by atmospheric oxidation, present in the solution electrolyzed. It was feared at first that, if benzoic acid were present, hydrogen from the benzoic acid would be introduced into the benzaldehyde with the formation of compounds such as benzyl alcohol and hydrobenzoin, instead of the desired introduction of ethyl groups. It was found during the course of the work, however, that even when benzoic acid and water were carefully excluded, hydrobenzoin was nevertheless a product of the electrolysis. On the other hand, it was found that the yield of the ethyl ether of ethylphenyl carbinol was not appreciably decreased by the presence of small amounts of benzoic acid in the solution electrolyzed and hence in later experiments benzaldehyde was distilled into the cell without the use of nitrogen.

Ethyl iodide (80 cc. or 1 mole) was added slowly through the dropping funnel K to the cathode compartment of the cell. During the addition of the ethyl iodide, the cell was shaken gently to secure mixture of the iodide with the benzaldehyde. Ten cc. of ethyl iodide was added in the same way to the anode solution; 15 cc. of triethylamine was then added in the same way to the cathode solution and 5 cc. to the anode solution. After an hour, the ethyl iodide and triethylamine had reacted completely to form tetra-ethylammonium iodide and the cell was ready for the electrolysis.

Purification of Materials.—Benzaldehyde was freed from benzoic acid by shaking with sodium carbonate solution and was then fractionally distilled, a 4-bulb Young still-head being used. Only the main fraction boiling at 178.5–179.0° (corr.) at 760 mm. pressure was used in this work. The benzaldehyde recovered by distillation of solutions which had been electrolyzed (see below) and by decomposition of the bisulfite addition compound with sodium carbonate (see below) was purified in the same way by distillation and used again. Immediately before use the benzaldehyde was shaken with sodium carbonate solution to remove the benzoic acid formed during standing, by atmospheric oxidation. It was then shaken with water to remove the sodium carbonate and transferred to the apparatus as quickly as possible to avoid further oxidation.

Ethyl iodide was washed with sodium carbonate solution, dried over calcium chloride, and distilled through a 12-bulb Young still-head. The fraction boiling at 72.0–72.5° (corr.) at 760 mm. pressure was used. It was kept in brown bottles over calcium chloride in a dark place. Methyl iodide was similarly purified and preserved. It boiled at 44.5–45.0° (corr.) at 760 mm.

Triethylamine was distilled from sodium. The fraction boiling at 88.5–89.0° (corr.) at 760 mm. pressure was kept over sodium for use.

The Electrolysis.—The cell was arranged in series with a bank of lamps and a rheostat. By making the total resistance much greater than the resistance of the cell, the current through the cell could be kept fairly constant even though the resistance of the cell changed. It was therefore not necessary to give the cell constant attention. The current was kept at 0.5 ampere and the quantity of electricity used was usually about one faraday (26.8 ampere-hours). The electrolysis therefore lasted about two days. A difference of potential of 15–30 volt was usually necessary. By connecting a voltmeter across the terminals of the cell immediately after the current had been discontinued, a back e.m.f. of 1.2–1.0 volt was observed, which decreased to almost zero in a few minutes.

During the course of the electrolysis, the solution surrounding the cathode usually became brown, due to a slight diffusion of iodine from the anode solution through the diaphragm. Gas usually formed in bubbles on the cathode and was led out of the cell through the funnel J and collected and measured in an azotometer. After the electrolysis had proceeded for a time, tetra-ethylammonium iodide crystallized out of the cathode solution upon the electrode and the bottom of the cell. At the same time, the conductivity of the cell decreased, indicating that the concentration of electrolyte in the anode solution had decreased. More ethyl iodide and triethylamine were therefore added to the anode solution from time to time. This caused the conductivity of the cell to increase to its original value. A decrease in the concentration of tetra-ethylammonium iodide in the anode solution during the electrolysis was to be expected. More iodide ions were removed from the anode solution by oxidation to iodine or by precipitation as cuprous iodide than were supplied to the anode solution by migration through the diaphragm from the cathode side. Furthermore, tetra-ethylammonium ions were removed from the anode solution by their migration through the diaphragm into the cathode solution. On the other hand, the concentration of tetra-ethylammonium iodide in the cathode solution was increased during the electrolysis by migration of tetra-ethylammonium ions from the anode solution into the cathode solution and by the formation from ethyl iodide of iodide ions, of which only part migrated into the anode solution. Since the cathode solution was nearly saturated at the beginning of the electrolysis, tetra-ethylammonium iodide soon crystallized.

At the end of the electrolysis the tape covering the joint in the outer bottle B was removed, the glue was softened by directing a jet of steam against the crack, and the upper part of the bottle was raised so that the wire connecting the cathode with its lead-wire at the top of the cell could be cut. The upper part of the outer bottle B with the inner bottle A and the anode attached could then be removed.

Estimation of Free Iodine.—An aliquot part of the cathode solution was distilled with steam to separate the iodine from dark brown, nonvolatile substances. The quantity of iodine in the distillate was then determined by titration with a standard thiosulfate solution. The same procedure was used for the estimation of free iodine in the anode solution,

Removal of Ethyl Iodide.—The cathode solution was distilled with steam until a sample of the distillate gave no residue of ethyl iodide when treated with sodium bisulfite solution. The whole of the distillate, containing unchanged ethyl iodide and benzaldehyde, was then treated with an excess of a solution of sodium bisulfite. The residue from this treatment was distilled, the portion distilling below 75° representing the ethyl iodide which was not consumed by the electrolysis. The portion which did not distil below 75° was united with the remainder of the cathode solution, from which ethyl iodide and some benzaldehyde had been removed by steam distillation.

Removal of Benzaldehyde.—After the removal of ethyl iodide as described above, the remainder of the cathode solution was washed with sodium bicarbonate solution to remove benzoic acid, then with sodium thiosulfate solution to remove iodine, and was finally distilled under reduced pressure. Most of the material distilled at 61–62° at 13 mm. pressure (73–74° at 20 mm.) and was practically pure benzaldehyde, since a sample treated with sodium bisulfite gave no appreciable residue. The material which did not distil below 62° was treated with a slight excess of sodium bisulfite and enough water to keep the sodium bisulfite-benzaldehyde addition compound in solution at 100°. The mixture was then transferred to a separatory funnel which had been warmed in an oven at 120°. The lower, aqueous layer containing the benzaldehyde-bisulfite addition compound in solution was drawn off before it started to crystallize. In this way most of the benzaldehyde was removed without the use of an inconveniently large volume of bisulfite solution. The upper, nonaqueous layer was treated with more sodium bisulfite in the cold to remove the last traces of benzaldehyde, for the benzaldehyde-bisulfite addition compound is somewhat decomposed into its components at 100°.

Separation of Reaction Products.—The mixture of reaction products, from which iodine, ethyl iodide and benzaldehyde had then been removed, was distilled with steam. The distillate, after the removal of water, consisted of a liquid which had an odor of the ethyl ether of ethylphenyl carbinol and of ethyl benzoate and which sometimes also had a lachrymatory effect, especially when warmed. Sometimes lozenge-shaped crystals appeared in the condenser during steam distillation. The portion of the reaction products which were not volatile with steam consisted of a dark brown, tarry mass which constituted 80–90% by weight of the total reaction product.

Stilbene.—The crystalline material sometimes obtained by steam distillation was recrystallized from dil. alcohol, forming beautiful, iridescent lozenges that melted at 123–124° (corr.). A mixture of this material with a known sample of stilbene melted at the same temperature. The substance is therefore stilbene.

The Iodide.—The liquid obtained by steam distillation was allowed to stand with dimethylaniline at room temperature for several days. When the liquid originally had a lachrymatory effect, white needles were deposited and the liquid no longer affected the eyes. When, on the other hand, the liquid originally had no lachrymatory effect, there was no apparent reaction with dimethylaniline. The crystals were filtered off and washed with ether, in which they were insoluble. The substances was very soluble in water and gave a strong test for iodide ion with silver nitrate. After recrystallization from dil. alcohol, it melted at 152° (corr.), with the formation of two immiscible layers. Further recrystallizations did not raise the melting point. Not enough of the purified material was available for an analysis. Phenylbenzyl-dimethylammonium iodide, prepared from benzoyl iodide and dimethyl aniline, melts[5] at 164.5°. The lachrymatory iodide obtained from the electrolysis product is therefore not benzyl iodide.

The Benzoate.—The liquid from which the iodide had been removed was washed with dil. sulfuric acid to remove the excess of dimethylaniline and was then boiled for two hours with dil. sodium hydroxide solution. Acidification of the alkaline aqueous solution produced a copious, white precipitate. Recrystallized from hot water, this was identified as benzoic acid by a mixed melting point. The residue from the saponification no longer had the odor of ethyl benzoate.

The Ethyl Ether of Ethylphenyl Carbinol.—The residue from the saponification, distilled at 20 mm. pressure, gave a principal fraction boiling at 85–90° (80–85°, at 15 mm.), a smaller fraction boiling at 90–100°, and some residue. The principal fraction amounted to about 1 g., or 2% of the total weight of the reaction products formed at the cathode.

Anal. (fraction boiling at 85–90°). Calc. for $C_{11}H_{16}O$: C, 80.42; H, 9.82. Found: C, 80.15, 80.28; H, 9.98, 9.77.

As a check, the ether was also prepared by first preparing the phenylethyl carbinol

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[5] Jones, *J. Chem. Soc.*, **83**, 1409 (1903).

from benzaldehyde and ethyl bromide by means of the Grignard reaction and then alkylating the carbinol with ethyl sulfate and sodium hydroxide. The ether obtained in this way possessed the same boiling point (85–90° at 15 mm.) and gave upon analysis 80.32% of carbon and 9.77% of hydrogen. The ethyl ether of ethylphenyl carbinol is a colorless, mobile liquid with a characteristic, pleasant, persistent odor.

The fraction boiling at 90–100°, which contained principally the ethyl ether, was boiled with a solution of potassium dichromate and sulfuric acid. The product of this oxidization was dissolved in ether and washed with sodium carbonate solution to remove the benzoic acid which was also formed. On evaporating the ethereal solution, a liquid with the odor of propiophenone was obtained. This was warmed gently with an excess of semicarbazide hydrochloride and sodium acetate in aqueous solution. After a time, a mass of white scales separated. These were filtered off, washed with petroleum ether, in which they were insoluble, and crystallized to constant melting point from dil. alcohol. The purified material formed large, irregular plates which melted at 178° (corr.). The melting point of propiophenone semicarbazone is 173–175°, according to Stobbe.[6]

Attempts to isolate crystalline substances from the portion of the electrolysis product which was not volatile with steam by cooling with ice and salt or with liquid air and alcohol were fruitless. Distillation of the material at 0.1 mm. pressure gave a further quantity of stilbene as the only crystalline product and did not give promise of separating the mixture by fractional distillation. Two of the components could be isolated, however, by extracting the material repeatedly with large quantities of boiling water, then extracting the aqueous solution with ether and evaporating the ether solution.

Hydrobenzoin.—The material thus obtained was crystallized from alcohol, forming lozenge-shaped crystals; m. p., 135° (corr.). It gave a strong odor of benzaldehyde and benzoic acid when oxidized with potassium dichromate and sulfuric acid. It was oxidized to benzil, m. p. 95° (corr.), by concd. nitric acid. It was further shown to be hydrobenzoin by conversion into the diacetate by warming with an excess of acetyl chloride. This formed large prisms when crystallized from alcohol and melted at 131–133° (corr.), corresponding to 133–134° given in the literature.[7]

Unsymmetrical Diphenyl-ethylene Glycol.—The mother liquor from the crystallization of the hydrobenzoin gave needle-shaped crystals on evaporation. By recrystallization several times from hot water, needles melting 121–122° (corr.) were obtained. Recrystallization from a mixture of benzene and petroleum ether gave square plates with the same melting point and properties as the needles. The substance gave a strong odor of benzophenone when oxidized with potassium dichromate and sulfuric acid. When heated dry, it had an odor of benzophenone and formaldehyde. This property, the melting point, and crystalline form agree with the data given in the literature for unsymmetrical diphenyl-ethylene glycol.[8] In some experiments, no glycol could be isolated.

Anal. Subs., 0.1017: H_2O, 0.0587; CO_2, 0.2924. Calc. for $C_{14}H_{14}O_2$: C, 78.68; H, 6.46. Found: C, 78.46; H, 6.59.

The residue from which the glycols had been extracted amounted to more than half of the reaction product obtained from the cathode solution.

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[6] Stobbe, *Ann.*, **321**, 103 (1902).

[7] Fittig, *Ann.*, **168**, 67 (1873).

[8] Paal and Weidenkaff, *Ber.*, **39**, 2063 (1906).

This tarry material was not appreciably affected by boiling with potassium dichromate and sulfuric acid. It was oxidized by hot, concd. nitric acid to a non-crystallizing, neutral oil and a mixture of poorly crystallizing acids which could not be separated by fractional crystallization.

The Gas.—Unfortunately, the sample of the gas formed at the cathode which was saved for analysis became diluted with air: 10.2 cc.- and 8.0 cc.-portions, mixed with air and exploded, suffered contractions of 11.7 cc. and 8.8 cc., respectively, with the formation of 10.8 cc. and 8.1 cc. of carbon dioxide. The ratio of the contraction due to explosion to the volume of carbon dioxide formed is 1.08 in each case. This ratio calculated for ethylene is 1.00, for ethane 1.25, for butane 0.87. These results indicate that the gas contained 55% of ethylene mixed with air. This is confirmed by the fact that 5.5 cc. of a 10.0cc. sample of the gas was absorbed in bromine water.

In some experiments, no formation of gas could be observed on the cathode and the pressure within the cell did not increase during the electrolysis. In other experiments, gas was formed at the rate of 20 to 100 cc. per hour with a current of 0.5 amp.

The Anode Solution.—The asbestos diaphragms often used permitted some diffusion between anode and cathode solutions. At the end of the electrolysis, some iodine was found in the cathode solution and small quantities of the ethyl ether of ethylphenyl carbinol, hydrobenzoin, etc., in the anode solution. The quantity of iodine and iodide found in the anode solution was 30–40% of the amount required by calculation of the quantity of electricity used. A large part of the iodine formed at the anode diffused through the diaphragm and was partly reduced to iodide again at the cathode. Part of the current at the cathode was therefore used to reduce the iodine instead of the benzaldehyde. The yield of the reduction products of benzaldehyde was therefore also decreased.

When the diaphragm was made thick enough to prevent this diffusion, the resistance of the cell became so great that only a small current could be used and reaction products were not formed in sufficient quantities to be carefully investigated.

One such electrolysis was carried out on a small scale, using a lead anode and a thick cup of unglazed porcelain as a diaphragm. The quantity of electricity used was 1.70 ampere hours; 1.9 g. of iodine (determined by titration with thiosulfate solution) was found in the anode solution, accounting for 0.40 ampere-hour and 10.95 g. of lead iodide, accounting for 1.27 ampere-hours. After the removal of iodine, the anode solution gave no appreciable residue when treated with sodium bisulfite and was therefore practically pure benzaldehyde. It may therefore be concluded that iodine and iodide are the only products formed at the anode and that the ethyl ether of ethyphenyl carbinol, hydrobenzoin, etc., are formed only at the cathode.

Some electrolyses were carried out in cells filled with air instead of nitrogen, so that some benzoic acid was present, due to atmospheric oxidization of benzaldehyde. Other electrolyses were run in cells in which no diaphragm was used to separate anode and cathode solutions. Neither of these modifications seemed to have much effect upon the proportion of the ethyl ether of ethylphenyl carbinol in the organic product of the reaction. Although the ethyl ether was formed in each electrolysis of benzaldehyde and ethyl iodide, not all of the other cathode products already described (see p. 2256) could be found in each case. No relation could be discovered between the conditions of the experiment and the appearance or non-appearance of any reaction product. Since in this research the principal interest was in the formation of the ethyl ether of ethylphenyl carbinol and since this was always formed, it was not thought advisable at this time to study the influence of conditions upon the formation of the other, less important products of the electrolysis.

In some cases the benzaldehyde solution, standing in contact with the copper electrodes before the electrolysis was started, became green. This was undoubtedly due to the formation of benzaldehyde-copper,[9] $C_{14}H_{12}O_2Cu$. It was thought possible that some of the reaction products obtained from the solution which had been electrolyzed might arise from the reaction of the benzaldehyde-copper with ethyl iodide and not from the action of the current. To test this point, a benzaldehyde solution of ethyl iodide and tetra-ethylammonium iodide, of the same concentration as that electrolyzed, was allowed to stand in contact with copper gauze for several months. At the end of this time, the solution was treated with an excess of sodium bisulfite solution. Since only unchanged ethyl iodide remained after the removal of the benzaldehyde, it was concluded that benzaldehyde-copper and ethyl iodide do not react under the conditions of the electrolysis.

Electrolysis of a Solution of Methyl Iodide in Benzaldehyde.—A benzaldehyde solution of methyl iodide and potassium iodide was electrolyzed between platinum electrodes in a small cell without a diaphragm. The resulting solution was worked up in the same way as the solutions obtained in the larger experiments with ethyl iodide, (see pp. 2262, 2263) and yielded a liquid with an odor like that of the ethyl ether of ethylphenyl carbinol obtained by the use of ethyl iodide. It was oxidized by potassium dichromate and sulfuric acid to a liquid with an odor like that of acetophenone. This formed a semicarbazone which melted at 196° (corr.). A mixture of this with acetophenone semicarbazone (m. p., 201°, corr.) melted at 200° (corr.). The highest melting point given[10] for aceto-

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[9] Bernoulli and Schaff, *Helv. Chim. Acta*, **5**, 721 (1922).

[10] Schlotterbeck, *Ber.*, **40**, 482 (1907).

phenone semicarbazone is 201° (corr). Stilbene was also identified as a product of this electrolysis.

Electrolysis of a Solution of Methyl Iodide in Benzonitrile.—Benzonitrile was distilled directly from phosphorus pentoxide into a small cell with platinum electrodes and no diaphragm. It was then saturated with potassium iodide by shaking, methyl iodide was added, and the solution was electrolyzed. The gas which formed on the cathode was shown to be principally methane by the method described on p. 2265. At first, the gas was formed in the full yield required by the current used, 0.5 mole per faraday. Later, as iodine was formed at the anode and diffused to the cathode, part of the current at the cathode was used in reducing the iodine back to iodide and the current yield of the gas accordingly decreased. The total volume of gas formed, however, was equivalent to the amount of iodine in the cell at the end of the electrolysis. Apparently, then, all the current at the cathode reduced iodine to iodide or formed methane. After the removal of iodine and unchanged methyl iodide, the electrolyzed solution was boiled with sodium hydroxide solution. Practically all the liquid was dissolved and the aqueous solution gave only benzoic acid on acidification.

Electrolysis of a Solution of Methyl Iodide and Propionitrile.—Propionitrile substituted for benzonitrile in the above experiment gave entirely similar results.

Electrolysis of a Solution of Methyl Iodide in Acetone.—Acetone, prepared from the bisulfite addition product and dried with potassium carbonate, gave methane when its potassium iodide-methyl iodide solution was electrolyzed. Little iodine was found at the end of the electrolysis, most of it apparently reacting to form a black, tarry substance. There was no evidence of the formation of the expected tertiary-butyl methyl ether.

Summary

The reactions taking place when a solution of benzaldehyde containing ethyl iodide and tetra-ethylammonium iodide is electrolyzed have been investigated. One of the products of the electrolysis has been shown to be the ethyl ether of ethylphenyl carbinol, a substance never before prepared. The reaction by which this compound is formed, involving the electrolytic introduction of two ethyl groups into the benzaldehyde molecule, has been discussed and its analogy with the Grignard reaction and to ordinary reduction reactions has been pointed out.

Preliminary work has been carried out indicating that a similar reaction takes place in the case of benzaldehyde and methyl iodide, with the formation of the methyl ether of methylphenyl carbinol.

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