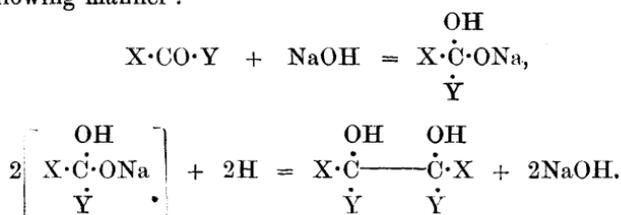


CXLIX.—*Electrolytic Reduction. I. Aromatic Aldehydes.*

By HERBERT DRAKE LAW.

THE first account of the reduction products of the aromatic aldehydes obtained by means of an electric current was given by Kaufmann (*Zeit. Elektrochem.*, 1895, 2, 365), who showed that benzaldehyde in a sodium bisulphite solution yielded a mixture of a small quantity of hydro- and isohydro-benzoin at the cathode. At a later date the same author stated that a much better yield was obtained when alcoholic solutions were used, employing sodium hydroxide as electrolyte (*Zeit. Elektrochem.*, 1898, 4, 461). Benzoin, benzil, and acetophenone all gave products similar to the above, the reaction taking place presumably in the following manner :



In 1902, Elbs and Brand (*Zeit. Elektrochem.*, 8, 784) obtained similar results with a number of ketones, but here the reaction often proceeded a stage further and the alcohol corresponding to the aldehyde was produced.

In the present work the first experiments were conducted with

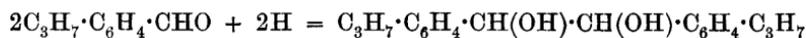
benzaldehyde in alcoholic solutions, using potassium hydroxide as the electrolyte. An almost theoretical yield of *isohydro-* and *hydro-benzoin* was obtained together with a very small quantity of resinous matter, which was, however, not sufficient to interfere with the reaction. The introduction of such groups as $-\text{OH}$, $-\text{OCH}_3$, $\begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{CH}_2$ into the benzene nucleus was found also to interfere to no considerable extent with the main reaction. Such aldehydes as furfural and cinnamaldehyde, which contain an unsaturated carbon atom, yielded nothing but a resinous product. The latter agrees with the anodic phenomenon and confirms the statement already made (*Trans.*, 1906, 89, 1437), that unsaturated aldehydes polymerise under the influence of an electric strain. Benzoin, piperonyloin, anisoin, and cuminoin all yield similar products, of which tetraphenylerythritol may be taken as a type. The appearance of such substances as anisil is remarkable, however, and no explanation is given.

Description of the Apparatus.

Throughout this research the same form of apparatus was used. The cathode compartment consisted of a cylindrical porous pot, having a capacity of 120 c.c. This was thoroughly cleaned by forcing first a dilute solution of sodium hydroxide and then dilute sulphuric acid through the walls to remove the soluble metallic impurities. Such a porous pot was fitted with a treble-bored rubber stopper carrying a dropping funnel, a short delivery tube, and a short glass tube to hold the electrode. In each case the cathode was bent in the form of a cylinder, and was fixed in position by means of sealing-wax; it had an area of 17.5 sq. cm. on one side. The hydrogen escaping from the apparatus was conducted to a graduated measuring cylinder inverted over water, and the volume read off from time to time. The anode compartment was a beaker about 10 cm. deeper than the porous pot, containing a stout platinum wire to act as anode. Three such sets of apparatus were coupled in series with an adjustable rheostat and twelve accumulators. One piece of apparatus was used as a hydrogen coulombmeter and the other two for reduction purposes, one being a duplicate of the other. In this way the total hydrogen reacting at the cathode could be measured from the difference in the water levels of the coulombmeter and the reduction apparatus. In many cases the product was precipitated during the experiment on to the cathode, but did not interfere with the reaction as is the case in acid solutions.

Cuminaldehyde.

The cathode solution measured 75 c.c. and contained 5 grams of cuminaldehyde, 50 c.c. of absolute alcohol, 5 per cent. of potassium hydroxide, the remainder being distilled water. The cathode was either polished nickel or platinum, and the current of 1 ampere was continued for two to three hours. At the end of the experiment 360 c.c. of hydrogen had been absorbed, whilst the theoretical amount calculated from the equation



is 375 c.c. No solid had separated and the cathode solution was, therefore, precipitated by water. The product weighed nearly 5 grams. This was washed with hot light petroleum and filtered from the insoluble portion. The latter weighed 2 grams, and after crystallisation from heavy petroleum melted finally at 137°. This was found to be hydrocuminoïn. The portion soluble in light petroleum was recovered and recrystallised several times and in each case the final product was the above substance melting at 137°. The residue always melted at 90—92°, but continued to yield a further quantity of the substance of high melting point on further purification. This may have been due to the gradual conversion of the one into the other during the process of crystallisation. The substance melting at 90—92° gave the following result on analysis:

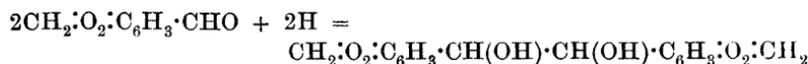
0·1017 gave 0·2990 CO₂ and 0·0757 H₂O. C = 80·14; H = 8·27.

C₂₀H₂₆O₂ requires C = 80·53; H = 8·72 per cent.

This is, therefore, probably *isohydrocuminoïn* containing a little hydrocuminoïn. In addition to these two substances there was formed also a small quantity of resinous matter which, on long standing, deposited a little more mixed product.

Piperonaldehyde.

The solution in the cathode compartment contained 5 grams of piperonaldehyde, 38 c.c. of absolute alcohol, 5 per cent. of potassium hydroxide, and the whole was made up to 75 c.c. with water. The cathodes were either polished nickel or platinum. A current of 1 ampere was passed through this solution for three to four hours. At the end of that time a yellow solid had separated from the solution, which was then filtered. The amount of hydrogen absorbed during this process was 350 c.c., whilst that required by the equation



is 370 c.c. It was expected, therefore, that an almost theoretical yield of hydropiperonyloin had been obtained. The part remaining in the alcoholic solution was precipitated by means of water and filtered. The two portions obtained in this way weighed almost 5 grams and were present in equal quantities. The yellow solid which had separated during the experiment was crystallised twice from amyl alcohol and the melting point was found to be 200°. This substance is soluble with difficulty in organic solvents, and is undoubtedly hydropiperonyloin, the melting point of which is given as 202°. The other portion was crystallised twice from benzene and the melting point was found to be 132°. This substance is therefore *isohydropiperonyloin* (m. p. 132°). Both the above compounds were first prepared by Fittig and Remsen (*Annalen*, 1871, 159, 130) by reducing piperonal with sodium amalgam.

Anisaldehyde.

The solution at the cathode contained 5 grams of anisaldehyde, 38 c.c. of alcohol, 5 per cent. potassium hydroxide, and the whole was made up to 75 c.c. with distilled water. The cathodes used were composed either of polished platinum or nickel. A current of 1 ampere was allowed to pass through the solution for two to three hours, at the end of which time 380 c.c. of hydrogen had been absorbed. According to the equation



410 c.c. are required, which is a very close agreement. At the end of the experiment, part of the product had separated and was removed by filtration from the alcoholic solution. The latter was poured into water to precipitate the soluble matter. These two portions were almost equal in weight, the total amount being 5 grams. The insoluble portion was crystallised twice from alcohol, when the melting point was found to be 170°. The other part, after being crystallised from a mixture of alcohol and water, and finally from benzene, melted at 113°. These two substances were therefore hydroanisoin (m. p. 168°) and *isohydroanisoin* (m. p. 110°) respectively (*Annalen*, 1871, 159, 130).

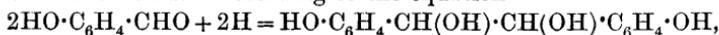
Vanillin.

In this case, it was quite essential to prevent the free access of air from the cathode compartment and to keep the temperature as low as possible with running water, otherwise the product was entirely resinous. The cathode solution measured 75 c.c., and contained 5 grams of vanillin and 5 per cent. of potassium hydroxide, the remainder being water. A current of 1 ampere was passed through this solution for two and a half to three hours, at the end of which time 380

c.c. of hydrogen had been absorbed, whilst only 370 c.c. were necessary for the production of hydrovanilloin. The cathodes, which were similar to those used in previous experiments, always became covered with a dark brown deposit. The cathode solution was acidified with hydrochloric acid and allowed to stand until no more crystals separated, and a product, amounting to 80 per cent. of the theory, was obtained. The crude substance always contained a quantity of resin, which was removed by washing with chloroform. The insoluble residue melted at 222° and was *hydrovanilloin*. No definite product was obtained from the resin, but it is probable that it contained some isomeric compound. The yield of pure hydrovanilloin was 45 per cent. of the theory.

Salicylaldehyde.

The product in this case is even more readily influenced by changes of the conditions than is vanillin. It is absolutely essential to exclude the free access of air during the experiment, and the best results were obtained with low current densities. The cathode solution contained 5 grams of salicylaldehyde and 5 per cent. of potassium hydroxide, the total volume of the solution being 75 c.c. In this case, no alcohol was required, the substance being readily soluble in the alkaline solution. A current of 0.2 ampere was used, and the whole apparatus was kept cool by means of cold water. The experiment was allowed to proceed until no more hydrogen was observed and was complete in eight to nine hours. According to the equation



410 c.c. of hydrogen are required to complete the reaction, whilst in an actual experiment 460 were absorbed. The mixture was diluted with water and several grams of potassium bicarbonate added. The solution was kept cool with ice or cold water and precipitated with dilute hydrochloric acid. It was found necessary to proceed in this manner, as acids stronger than carbonic acid caused the substance to darken considerably during the precipitation, and at the same time effected no separation of the two substances formed. The first portion precipitated was a white, amorphous powder which could not be obtained in a crystalline state. It was purified by dissolving in sodium hydroxide and reprecipitating with hydrochloric acid. It begins to soften at 122° and chars at 147° without melting.

0.1004 gave 0.2490 CO_2 and 0.0561 H_2O . C = 67.91 ; H = 6.21.

$\text{C}_{14}\text{H}_{14}\text{O}_4$ requires C = 68.29 ; H = 5.70 per cent.

The substance is therefore *hydrosalicyloin*, or a mixture of *isohydro-* and *hydro-salicyloin*. The yield was 70 per cent. of the theory.

The solution on standing for several days deposited a further quantity of a substance which, on being crystallised from dilute

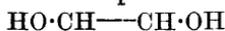
alcohol, melted at 113°. On analysis, the following results were obtained :

0.1015 gave 0.2950 CO₂ and 0.0481 H₂O. C = 79.26 ; H = 5.26.

C₁₄H₁₂O₂ requires C = 79.24 ; H = 5.66 per cent.

A molecular weight determination by the freezing-point method in benzene solution gave the values 197 and 196.

A compound of the above formula requires M.W. = 212, which agrees fairly closely with the experimental result. The substance, which is insoluble in caustic alkalis, is readily attacked by bromine, evolving dense fumes of hydrobromic acid. In this respect it behaves like the secondary alcohols of the benzene series, and from the method of preparation such a compound was to be expected. It is therefore



probably 9 : 10-dihydroxyphenanthrene,  .

Reactions similar to these will be investigated in the near future.

Furfurol.

This substance in alkaline solutions was completely converted into a semi-solid, tarry mass very closely resembling the product obtained by electrolytic oxidation. In sulphuric acid solution the mixture was often oily in appearance, and contained considerable quantities of furan carbinol, the main portion, however, always being of a resinous nature.

Cinnamaldehyde.

This unsaturated compound behaves exactly like furfurol, the main product being tar.

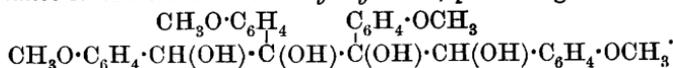
Anisoin.

Five grams of this substance were dissolved in 55 c.c. of alcohol, and the whole was made up to 70 c.c. with water. Sufficient potassium hydroxide dissolved in 5 c.c. of water was added to give a 5 per cent. solution. Complete solution was effected only by keeping the mixture warm, and then a beautiful purple solution was obtained. A current of 1 ampere was passed through this solution for eight hours, at the end of which time the reaction was complete. The cathodes used were either platinum or nickel. When the experiment was finished, part of the product had separated from the solution and was removed by filtration. This insoluble portion was dissolved in pyridine and fractionally precipitated. In this manner a white, flocculent mass was obtained which gave the following result on analysis :

0.1020 gave 0.2630 CO₂ and 0.0580 H₂O. C = 70.32 ; H = 6.32.

C₃₂H₃₄O₈ requires C = 70.33 ; H = 6.23 per cent.

The substance is therefore *tetra-anisylerythritol*, possessing the constitution



The portion still in solution was precipitated by pouring into water, when a yellow solid was obtained. This was washed several times with small quantities of boiling methyl alcohol, and from the first of these washings crystals of a yellow substance separated on cooling, but the latter portions gave a semi-solid mass which was only partially crystalline. These crystals melted sharply at 132° , and on analysis :

0.1016 gave 0.2667 CO_2 and 0.0512 H_2O . $\text{C} = 71.40$; $\text{H} = 5.58$.

Molecular weight in benzene solution = 251.

$\text{C}_{16}\text{H}_{14}\text{O}_4$ requires $\text{C} = 71.11$; $\text{H} = 5.18$ per cent., and M.W. = 270.

The substance is therefore anisil (m. p. 133°). The formation of this diketone at the cathode is difficult to explain ; it is certainly not a primary product of the reduction.

The semi-solid mass was not treated further as no crystalline product could be obtained. On long standing, further crystals of anisil were deposited, but these could not be removed completely.

The insoluble portion left after the washing with hot alcohol amounted to 35—40 per cent. of the whole.

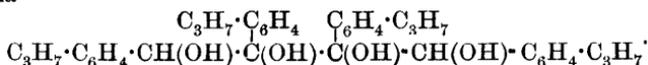
Cuminoin.

Five grams of this substance were dissolved in 55 c.c. of alcohol to which 7.5 c.c. of a 50 per cent. solution of potassium hydroxide were added, and the whole was made up to 75 c.c. with water. A purple solution was obtained which was kept warm in order to prevent part of the cuminoin from crystallising out. The cathode was composed of either polished platinum or nickel, and a current of 1 ampere was passed until no more hydrogen was absorbed. The reduction was complete in two to three hours, when part of the product had been precipitated from the solution. This portion, which amounted to 40 per cent. of the cuminoin employed, was dissolved in a mixture of hot alcohol and pyridine, and precipitated fractionally with water. In this manner a white, flocculent product was obtained, which, after drying on a porous plate, formed a white, semi-transparent, brittle mass resembling cellulose in appearance.

0.1010 gave 0.3030 CO_2 and 0.0808 H_2O . $\text{C} = 81.02$; $\text{H} = 8.88$.

$\text{C}_{40}\text{H}_{30}\text{O}_4$ requires $\text{C} = 80.81$; $\text{H} = 8.42$ per cent.

This substance is, therefore, *tetracuminylerythritol*, possessing the formula



It is soluble only in acidic and basic organic solvents, from which it can be precipitated as an amorphous powder melting at 210—212°. The filtrate from the crude product was poured into water, and 2 grams of a viscid, semi-solid mass were obtained. This was dissolved in alcohol, which was allowed to evaporate very slowly, and the solid matter separated from the resinous part. The former was then carefully crystallised from a mixture of pyridine and water, when a white, crystalline substance was obtained melting sharply at 81°. This proved to be cuminil (m. p. 84°), but the yield was very small.

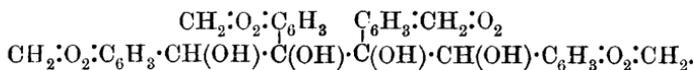
Piperonyloin.

Five grams of this substance were dissolved in 55 c.c. of alcohol, to which were added 7·5 c.c. of a 50 per cent. solution of potassium hydroxide. The mixture was then made up to 75 c.c. with distilled water, and warmed to keep the whole of the piperonyloin in solution. As the experiment proceeded, however, the whole remained dissolved, as the product is very soluble in alcoholic potash. The fresh solution was violet, but after the experiment was finished this had changed to yellow. When the reduction, which required from two to three hours, was complete, the whole was poured into water to precipitate the product, which amounted to 4·5 grams. This was dried and extracted with ether. The residue was a white, amorphous mass, quite insoluble in neutral organic solvents, but readily soluble in acetic acid or pyridine. It was purified by dissolving in a mixture of pyridine and alcohol, from which it was precipitated on cooling as a white, flocculent precipitate (m. p. 203—205°), resembling cellulose in appearance; yield, 35 per cent. On analysis:

0·1035 gave 0·2432 CO₂ and 0·0433 H₂O. C = 64·08; H = 4·65.

C₃₂H₂₆O₁₂ requires C = 63·79; H = 4·32 per cent.

This substance is therefore *tetrapiperonylerythritol*,



The portion soluble in ether gave, on evaporation, a viscid, yellow substance, which on standing in a vacuum set to a hard, brittle mass.

This was evidently a mixture of at least two substances, and from its deep yellow colour, and by analogy to anisoin and cuminoïn, it probably contains piperonil.

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