Electrolytic Reduction of Oximes,[1] III. Benzildioxime.

By

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ABSTRACT.

With the odject of tracing the cathodic reactions which bezildioxime undergoes under various conditions it was electrolysed both in the acid and in the alkaline solutions, using lead as the cathode. As was expected, reduction and hydrolysis take place side by side and many reduction-products were produced together. The ultimate reduction-product was diaminodiphenylethane which was obtained both in racemic and in meso-form. This fact is of interest when we compare it with purely chemical reduction which is reported to have produced the racemic form only. Other reduction-products such as diphenyloxyethylamine (normal and iso), tetraphenylaldine, benzoinpinacone, desoxybenzoinpinacone, toluylenehydrate (iso) and hydrobenzoin (normal and iso) are all derived from the hydrolysed dioxime by reduction. Of these substances, tetraphenylaldine may indeed be regarded as a reduction-product directly formed from the dioxime as Poionowska assumes. But the author considers it more likely to be produced from benzil-monoxime, and from this view point he put forward an assumption about the mechanism of the reaction which well accounts for the aldine formation, and establishes an analogy between the reduction of the carbonyl group on the one hand, and the oxime group on the other. It is to be noted here that the toluylenehydrate obtained by the reduction is not identical with that hitherto recorded in chemical literature. It is probably a new isomer.

The chief difficulty encountered by the electrolytic reduction of oximes is that, some of the oximes easily undergo hydrolysis at the cathode even in a dilute acid solution which is not capable of hydrolysing oximes without the aid of an electric current. The products of the hydrolysis thus become admixed with oximes, and are simultaneously reduced, making the result of the reduction exceedingly complicated.

As it was deemed to be interesting to see how hydrolysis and reduction take place in the case of dioximes, the cathodic behavior of benzildioxime was studied.

The electrolysis was conducted in an alcoholic solution acidified with

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[1] The first and second communications are to be found in these memoirs, A, **7**, 39 (1923).

sulphuric acid, using lead as the cathode. As was expected, reduction and hydrolysis took place side by side, and the following seven substances were produced as the reduction-products:

1. Diaminodiphenylethane (meso and racemic)
2. Diphenyloxyethylamine (normal and iso)
3. Tetraphenylaldine
4. Benzoinpinacone
5. Desoxybenzoinpinacone
6. Toluylenehydrate (iso)
7. Hydrobenzoin (normal and iso)

Of these seven products, diaminodiphenylethane is the only substance which may be regarded as the reduction-product directly produced from benzildioxime. It is note-worthy that in the electrochemical process diaminodiphenylethane is produced both in the meso and in the racemic forms, while by the purely chemical reduction conducted by Feist and Arnstein[1] it is reported to have been obtained only in the racemic form.
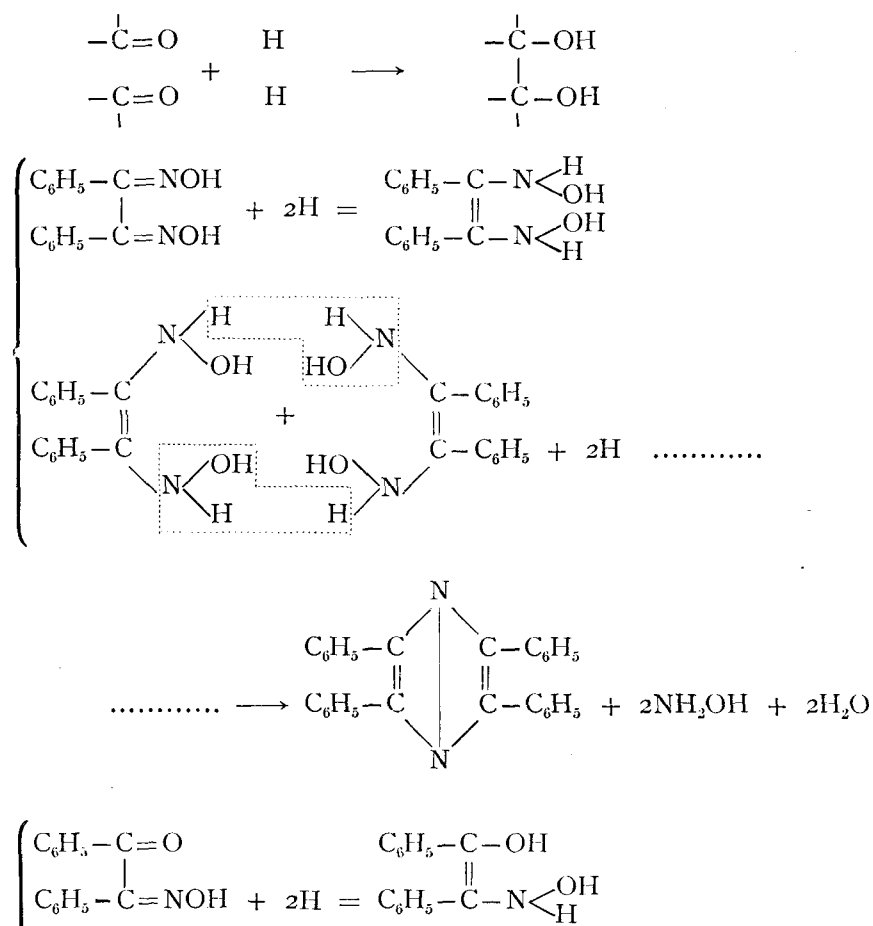
As to the formation of tetraphenylaldine, it is rather difficult to decide whether it is produced directly from the dioxime, or from the monoxime generated by hydrolysis of the dioxime. Hitherto it has generally been believed that both the dioxime and the monoxime yield tetraphenylaldine[2] when reduced thus :

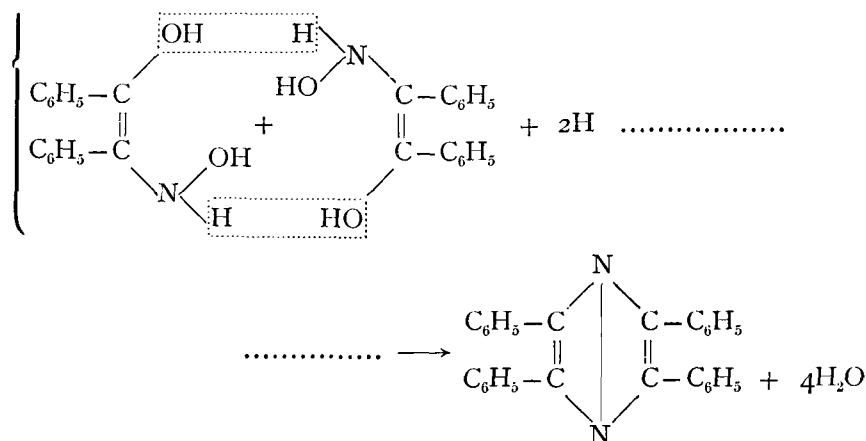$$\cdots\cdots\cdots + 2NH_3 + 2H_2O$$

$$\cdots\cdots\cdots + 4H_2O$$
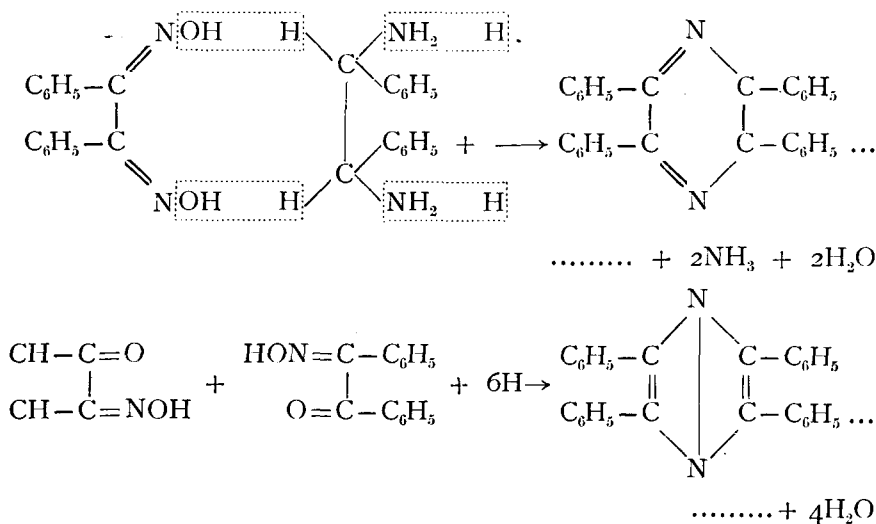
1 Ber. D. chem. Ges., **28**, 3167 (1895).

2 Goldschmidt and polonowska: *ibid.*, **20**, 492 (1887); Polonowska: *ibid.*, **21**, 488 (1888); Braun and Meyer: *ibid.*, **21**, 1269 (1888); Meyer and Auwers: *ibid.*, **21**, 3525 (1888); Feist and Arnstein: *loc. cit.*

By electrochemical reduction tetraphenylaldine is also produced from benzildioxime as well as from the corresponding monoxime, and its yield is always greater in the case of the dioxime. Though this fact seems to show that both oximes are equally liable to give tetraphenylldine by reduction, yet the above equation representing the formation of the aldine from dioxime is only hypothetical, and has no experimental verification for it, and as far as the author's experiments are concerned, such a reaction represented by the equation could not be brought about between benzildioxime and diphenyldiaminoethane. The author would submit the opinion that the formation of the aldine may well be explained on the assumption, that reduction of the dioxime or of the monoxime takes place just in the same manner as the carbonyl group is reduced to the pinacone, as is represented by the following scheme:

$$\begin{array}{c} -\overset{|}{C}=O \\ -\overset{|}{C}=O \end{array} \;+\; \begin{array}{c} H \\ H \end{array} \;\longrightarrow\; \begin{array}{c} -\overset{|}{C}-OH \\ -\overset{|}{C}-OH \end{array}$$

$$\begin{array}{c} C_6H_5-\overset{|}{C}=NOH \\ C_6H_5-\overset{|}{C}=NOH \end{array} \;+\; 2H \;=\; \begin{array}{c} C_6H_5-C-N{<}^{H}_{OH} \\ \parallel \\ C_6H_5-C-N{<}^{OH}_{H} \end{array}$$

$$\begin{array}{c} C_6H_5-C \\ \parallel \\ C_6H_5-C \end{array} \underset{N<^{OH}_{H}}{\overset{N<^{H}_{OH}}{<}} \;+\; \underset{^{HO}\diagdown N}{\overset{H\diagdown N}{HO\diagup}} \begin{array}{c} C-C_6H_5 \\ \parallel \\ C-C_6H_5 \end{array} \;+\; 2H \quad \dots\dots\dots$$

$$\dots\dots\dots \longrightarrow \begin{array}{c} N \\ C_6H_5-C\diagup\;|\;\diagdown C-C_6H_5 \\ \parallel \qquad \parallel \\ C_6H_5-C\diagdown\;|\;\diagup C-C_6H_5 \\ N \end{array} \;+\; 2NH_2OH \;+\; 2H_2O$$

$$\begin{array}{c} C_6H_5-C=O \\ \overset{|}{C_6H_5-C}=NOH \end{array} \;+\; 2H \;=\; \begin{array}{c} C_6H_5-C-OH \\ \parallel \\ C_6H_5-C-N{<}^{OH}_{H} \end{array}$$

$$\left\{ \begin{array}{l} C_6H_5-C \overset{OH}{\diagup} \quad\quad \overset{H}{\underset{HO}{\diagup}}N \diagdown \\ \quad\quad \| \quad\quad\quad + \quad\quad\quad \| \\ C_6H_5-C \diagdown_{\underset{H}{N}} OH \quad\quad \overset{C-C_6H_5}{\underset{HO}{\diagup}} \end{array} \right\} C-C_6H_5 \quad + \quad 2H \quad \dots\dots\dots\dots$$

$$\dots\dots\dots\dots \longrightarrow \begin{array}{c} N \\ C_6H_5-C \diagup \;\Big|\; \diagdown C-C_6H_5 \\ \| \quad\quad \| \\ C_6H_5-C \diagdown \;\Big|\; \diagup C-C_6H_5 \quad + \quad 4H_2O \\ N \end{array}$$

Perhaps it will be more satisfactory to assume, that the dioxime first changes to the monoxime by hydrolysis and then undergoes reduction, than to regard it as undergoing reduction directly. The fact that the dioxime gives the better yield of the aldine can also be explained without any contradiction, if we compare the rate of hydrolysis of both oximes. As the monoxime is far more easily hydrolysable than the dioxime, its large presence in the cathode solution at the commencement of the reaction must naturally be unfavourable for the aldine formation.

The ketonic group in benzilmonoxime is more readily reduceable than the oximido group, and as a consequence of this benzoinoxime is produced as the chief reduction-product of benzilmonoxime, and with it some diphenyloxyethylamine is also formed.

Benzoinpinacone, desoxybenzoinpinacone, toluylenhydrate and hydrobenzoin are all reduction-products of the hydrolysed oxime, and it will be out of place to describe their formation here in detail. Only it is to be noted that their formation is greatly influenced by various conditions. As for instance, when the electrolysis is conducted at a high temperature using a sulphuric acid as the cathode solution, neither hydrobenzoin nor toluylenehydrate is produced, while the formation of the pinacones increases. In a hydrochloric acid solution though toluylenehydrate and desoxybenzoinpinacone are not formed, tetraphenylaldine is produced with a better yield than in a sulphuric acid solution, together with some benzoinpinacone[1]. A caustic soda solution also favours the formation of tetraphenylaldine, but does not give toluylenehyd ate, hydrobenzoin or the pinacones.

1 Zinke: Lieb. Ann., **198**, 52 (1879).

Experimental Part.

The β–benzildioxime used in the experiment was prepared from the γ-variety according to the method of E. Beckmann and H. Köster.[1] It melted at 206°. To prepare the cathode solution 5 grams of the dioxime were dissolved in a solution consisting of 60 c. c. of alcohol. 40 c. c. of water and 5.5 c. c. of conc. sulphuric acid (1.83), and into this solution a lead plate of 100 sq. cm. was dipped as the cathode. As the anode solution a dil. sulphuric acid was taken and a platinum plate was made use of as the anode. At the end of the electrolysis, which was conducted by passing a current of 1.5 amp. for 6 hours at 16—18°, the cathode was found coated with minute crystals which on examination were proved to be a mixture of benzoinpinacone and desoxybenzoinpinacone previously obtained by the author by the reduction of benzoinoxime.[2]

The cathode solution was nearly neutralized with caustic soda and distilled, whereupon alcohol and a distillate which became milky on cooling were obtained. When alcohol was driven off from the milky distillate and left to stand over-night, fine long needle crystals separated out. Though the crystalline substance melts at 61—62° and resembles toluylenehydrate in every other respect, still the two are by no means identical, as a mixture of the former with pure toluylenehyrate prepared from benzoin according to the method of E. Knoevenagel and J. Arndts[3] shows a very much lower melting point, such as 36—39.° To ascertain what the substance could really be its composition and molecular weight were determined with the following results:

1. 0·0810 grm substance gave 0·2519 grm CO_2 and 0·0529 grm H_2O
2. 0.1123 〃 〃 〃 0·3494 〃 〃 〃 0·0711 〃 〃
3. 0·0836 〃 〃 〃 0·2593 〃 〃 〃 0·0530 〃 〃

	Found			Calc. for $C_{14}H_{14}O$
	1	2	3	
C	84·84	84·88	84·62	84·81%
H	7·31	7·08	7·09	7·12%

The molecular weight was determined by the cryoscopic method using benzene as the solvent.

Substance used 0·1740 grm, benzene taken 17 660 grm,
freezing point depressed 0·245°; mol. wt. observed 201,
that calculated for $C_{14}H_{14}O$ 198.

1 *Ibid.*, **274**, 19 (1893).
2 These Memoirs, A, **7**, 41 (1923).
3 Ber. D. chem. Ges., **35**, 1982 (1902).

From these results it may be clearly seen that the substance above obtained is toluylenehydrate, which belongs to a new variety isomeric but not identical with that already described in chemical literature.

On the surface of the liquid remaining in the flask after steam distillation a very small quantity of a yellowish oil was found to float, which gradually solidified to a yellow prism. The crystal melted at 95° and was identified to be benzil.

On standing the solution separated from the benzil a white precipitate (A) consisting of two parts, one of which is soluble and the other is insoluble in ligroin was obtained. The former when recrystallized from glacial acetic acid formed needle crystals melting at 245—246°, and on further examination it was confirmed to be tetraphenylaldine. The part insoluble in ligroin was found to contain hydrobenzoin, isohydrobenzoin, benzildioxime and monoxime. It was therefore treated with hot water, which dissolved the first two substances, leaving the last two unchanged.

The filtrate filtered from the white precipitate (A) was made strongly alkaline by adding caustic soda and extracted with ether.

The ether extract was saturated with carbon dioxide, and the precipitate thus formed was well washed with ether. As the precipitate might still contain some mono-amine, it was dissolved in hydrochloric acid, and the hydrochloric acid solution was made alkaline by caustic soda and extracted with ether. From the ethereal solution the diamine was again precipitated as a carbonate by passing carbon dioxide. The process was repeated once again in order to get rid off the mono-amine completely. Pure diphenyldiaminoethane carbonate was finally obtained, melting at 106°, and was easily transformed into the hydrochloride, $C_{11}H_{16}N_2,2HCl + 2H_2O$, melting at 248-250°, as F. Feist[1] describes.

In order to isolate free diamine its carbonate or hydrochloride was treated with caustic soda and extracted with ether, and the residue obtained by evaporating the ether from the ether extract was recrystallized from ligroin. The crystal which first crystallized out had a feathery appearance and showed a distinct difference from the plate crystal coming out slowly. The two crystals, the mixture of which had no definite melting point, were separated by fractional crystallization, and each was recrystallized from ligroin, when the feather-like crystal melting at 90°-93°, and the plate crystal with melting point of 118°-120° were obtained. The former was confirmed to be racemic diphenyldiaminoethane, and the latter that of the meso-form previously prepared by G. Groszmann[2]

1   Ber. D. Chem. Ges., **27**, 213 (1894).
2   *Ibid.*, **22**, 2298 (1889).

from amarine.

Thus it was made clear that by electrolytic reduction of benzildioxime, diphenyldiaminoethane of racemic-form, as well as that of meso-form is produced simultaneously, while purely chemical reduction[1] gives the racemic variety only. When the diamine combines with acids to form salts, its isomeric nature is lost, giving always the one and the same salt.

The free diamine was analysed by Kjeldahl's method with the following results:

0·1089 gram substance required 9·7 c.c. N/10 HCl

Found	Calc. for $C_{14}H_{16}N_2$
N 13·13	13·20%

The ethereal filtrate separated from diamine carbonate was evaporated to drive off the ether, and the residue was treated with ligroin. Tetraphenylaldine was isolated from the ligroin solution. The portion insoluble in ligroin was extracted with hot ligroin, and the residue obtained by evaporation of the ligroin was recrystallized from benzene, and by this process normal diphenyloxethylamine[2] (m. p. 160°-161°) and isodiphenyloxyethylamine (m. p. 129°) were obtained.

Several experiments conducted with the object of learning the influence of acid concentration, temperature, current density, etc., upon the electrolytic reduction gave no special results worthy of mention.

Use of a conc. alcoholic solution acidified with sulphuric acid as the cathode solution was not very effective to prevent hydrolysis, though the yield of diamine was thus increased slightly, and diamine was partly precipitated as a sulphate in the course of the electrolysis.

When a dil. alkaline solution was used as the catholyte, toluylenehydrate, hydrobenzoin and the pinacones were not formed, and at the same time the formation of diamine (racemic form only) and monoamine was found greatly decreased. This shows that neither the hydrolysis nor the reduction of benzildioxime successfully occur in an alkaline solution. In this solution more than 10% of the dioxime was seen to change into tetraphenylaldine.

Benzildioxime of α- and γ- form was expected to behave somewhat differently when compared with the β-variety. The result of the experiments, however, turned out quite contrary to the expectation, showing that the isomeric difference in the dioxime has nothing to do with reduction.

The author wishes to express his sincere thanks to Professor M. Matsui at whose suggestion the work was carried out.

1 F. Feist: *Loc. cit.*

2 These Memoirs, A, **7**, 39 (1923).