

Electroorganic Preparations

VI. Reduction of Compounds Containing the Azomethine group

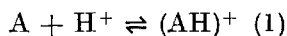
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The polarographic reduction in buffered medium of a number of ketimines, aniles, oximes, azines, phenylhydrazones, and semicarbazones have been investigated by use of controlled potential reductions. The number of electrons participating in the electrode reactions and the reduction products are reported and some indications of a probable reduction path are presented.

Compounds containing the azomethine group $>C=N-$ have mostly been of interest for polarography as a means of determining carbonyl compounds by converting them to a suitable azomethine derivative. Thus aliphatic ketones not reducible as such in buffered solutions can be determined as the ketimines^{1,2} or Girard hydrazones³⁻⁵. Other derivatives as hydrazones⁶, semicarbazones⁷, and oximes⁸⁻¹¹ have been investigated. Of these especially the oximes have received attention from various workers.

The polarographic behaviour of most of the compounds containing a carbon-nitrogen double bond have some features in common. Of the molecules in the equation



the $(AH)^+$ is reducible at a less negative potential than A and when $(AH)^+$ is removed from the reaction mixture by the reduction the equilibrium is forced to the right. The height of the polarographic wave is, therefore, in a certain pH-region determined by the rate of the recombination (1) of the molecules with the hydrogen ions¹². The phenomenon of recombination is found in the reduction of other compounds^{13,14}, but the special feature of many of the azomethine compounds is that in neutral and weakly alkaline solution the wave height at a certain pH is not constant but decreases at more negative potentials until another electrode reaction takes place. The phenomenon has been explained by the assumption that a change in the structure of the carbon-nitrogen double bond at the surface of the electrode caused by the lowering of the electrode potential lowers the rate of the recombination. As the subject

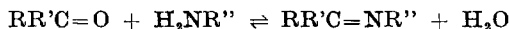
of the recombination in the polarography of oximes have been treated elsewhere^{9,10} only these introductory remarks have seemed warranted.

The purpose of the present work has been to investigate the electrode reactions which occur during the polarographic reduction of compounds containing a carbon-nitrogen double bond, and to this end a polarographic investigation of some aniles, oximes, amidoximes, azines, phenylhydrazones, and semicarbazones has been made together with preparative reductions at controlled potential of representatives from each group.

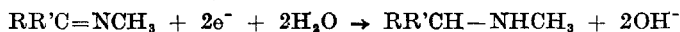
As the polarographic behaviour, especially the half-wave potentials, of the compounds is dependent upon the medium used all investigations were performed in 40 % alcohol containing 1 M potassium chloride as supporting electrolyte and the reducible compound in a concentration of 20 $\mu\text{g/ml}$. In order to facilitate the comparison of the compounds the limiting currents are reported for the concentration 10^{-3} M, which is calculated from the experimental data by assuming a linear dependence of limiting current on concentration.

Ket imines

Ketones as acetone and *cyclohexanone* give rise to a polarographic wave in a medium containing a primary amine or ammonia and a salt of the amine due to the reduction of the ketimine^{1,2} formed in the equilibrium:



Controlled potential reduction of a solution of *cyclohexanone* in a large excess of methylamine and methylamine hydrochloride showed that the reduction consumed two electrons per molecule *cyclohexanone* and the product was the expected N-methyl *cyclohexyl* amine.



Aniles

Only a few compounds of this class were investigated. Benzalaniline and salicylaldehyde anile were found to be too unstable both in alkaline and acid solution for a polarographic investigation. Benzophenone anile is rather unstable below pH 5, but at higher pH-values the stability is sufficiently high to allow both a polarographic investigation and a preparative reduction.

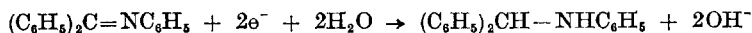
Table 1. Limiting currents in μA and half-wave potentials vs S.C.E. of benzophenone anile at different pH-values. Concentration 10^{-3} M. 0.01 % gelatine added as maximum suppressor.

pH	5.10		6.25		7.40		9.85		10.75		13	
	i_d	$-E_{\frac{1}{2}}$	i_d	$-E_{\frac{1}{2}}$	i_d	$-E_{\frac{1}{2}}$	i_d	$-E_{\frac{1}{2}}$	i_d	$-E_{\frac{1}{2}}$	i_d	$-E_{\frac{1}{2}}$
1. wave	2.2	0.82	2.4	0.89	2.4	0.96	4.8 ^a	1.10	4.8	1.13	2.4	1.21
2. wave	2.6	1.08	2.4	1.07	2.2	1.07					2.2	1.58

^a slight tendency to minimum.

The polarographic behaviour of benzophenone anile is similar to that of benzophenone in that two waves are found at lower pH values and only one at higher values (Table 1). As for benzophenone the first wave is pH-dependent, whereas the second one is not, and the combined wave is less dependent upon pH than the first one. The half-wave potentials of the anile are, however, about 0.3 V more positive than those of benzophenone, and whereas the two waves of benzophenone merge about pH 5 the waves of the anile merge about pH 9. Furthermore, there are found two waves in strongly alkaline solution for the anile, which is not the case for benzophenone. In the pH-region 9—12 a small minimum is found about -1.5 V; this is similar to that found for oximes and hydrazones.

Controlled potential reduction at pH 10 showed that the electrode reaction was a two electron reduction and the isolated product was benzhydrylaniline.

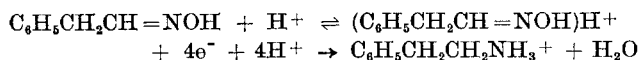


Attempts to reduce the anile at the plateau of the first wave at pH 6 were unsuccessful due to the difficulties of obtaining sufficient buffering in a medium in which the anile was appreciably soluble.

Oximes

Unconjugated oximes. The oximes of the following unconjugated carbonyl compounds were investigated polarographically: *Isobutyraldehyde*, phenylacetaldehyde, and benzylacetone (Table 2). They all show a single pH-dependent wave in acid solution and the height of the wave decreases at higher pH-values and disappears in alkaline solution. The polarographic wave shows, however, no minimum at higher pH-values.

Preparative reductions of *isobutyraldoxime* and phenylacetaldoxime showed that the electrode reaction was a four electron reduction, and from the latter reduction phenylethylamine was isolated.



α,β -Unsaturated oximes. Oximes of the following α,β -unsaturated carbonyl compounds were investigated polarographically: Crotonaldehyde, mesityloxide, carvone, testosterone propionate, cinnamaldehyde, and benzalacetone. The polarographic behaviour of these oximes were rather different (Table 2).

Crotonaldoxime shows in acid solution a single pH-dependent wave with the height determined by the rate of the recombination. About pH 8 the first wave disappears without showing minima and a second wave of nearly the same height as the wave in strongly acid solution appears. The half-wave potentials of this wave is approximately independent of pH. The wave is probably due to the reduction of the unprotonated crotonaldoxime. This wave disappears in strongly alkaline solution which might be explained by the formation of the more difficultly reducible oxime anion $\text{R}-\text{NO}^-$. Controlled potential reduction in weakly acid solution showed the electrode reaction to be a four electron reduction.

Table 2. Limiting currents in μA and half-wave potentials vs S.C.E. of some oximes and N-benzylhydroxylamine. Concentration 10^{-3} M. 0.01 % gelatine added as maximum suppressor.

pH	1.05		3.55		5.20		7.40		9.80		13	
	i_d	$-E_{1/2}$	i_d	$-E_{1/2}$	i_d	$-E_{1/2}$	i_d	$-E_{1/2}$	i_d	$-E_{1/2}$	i_d	$-E_{1/2}$
Compound												
Isobutyraldoxime	9.9	1.08	10.0	1.27	2.6	1.37	—	—	—	—	—	—
Phenylacetaldoxime	9.8	0.92	9.3	1.08	2.8	1.28	—	—	—	—	—	—
Benzylacetoneoxime	d		7.4	1.34	d		—	—	—	—	—	—
Crotonal- aldoxime	12.3	0.90	12.3	1.06	10.5	1.17	1.2	1.26	—	—	—	—
Mesityloxi- d									10.3	1.72	—	—
oxime	10.3	1.01	10.3	1.16	8.3	1.25	0.9	1.33	—	—	—	—
Carvone oxime	5.5	0.84	10.5	1.05	9.5 ^a	1.16	2.8 ^a	1.25	—	—	—	—
Testosterone propionate oxime	2.9	0.75	2.7	0.89	3.1	1.04	1.0	1.12	0.2	1.25	—	—
<i>anti</i> -Cinnam- aldoxime	3.1	0.99	2.9	1.09	3.9	1.22	4.0 ^a	1.22	—	—	—	—
<i>syn</i> -Cinnam- aldoxime	10.5	0.69	10.7	0.86	10.7	1.00	b		8.3	1.40	6.7	1.57
Benzalacetone oxime	10.7	0.70	10.7	0.87	9.8	1.00	b		5.7	1.49	—	—
<i>anti</i> -Benz- aldoxime					1.9	1.40			3.8	1.76	0.6	1.60
<i>syn</i> -Benz- aldoxime	9.5	0.75	9.3	0.92	9.0	1.03	b		1.7	1.42	—	—
N-Benzyl hydroxylamine			3.4	1.29	4.0	1.32			6.4	1.56	5.0	1.65
<i>p</i> -Aminoaceto- phenone oxime	c	0.7	9.2	0.92	6.2	1.08	0.9	1.20	—	—	—	—
<i>p</i> -Dimethylamino- benzaldoxime	c	0.7	9.2	0.92	5.3	1.08	0.2	1.15	8.0	1.62	6.7	1.72
							1.0	1.60	1.4	1.61	0.6	1.69
	—		—		d		d		—3.8	0.11	—4.0	0.47
	8.9	0.96	9.0	1.14	8.9	1.24	3.6 ^a	1.34	—	—	—	—
	10.0	0.80	9.8	0.97	10.2	1.07	5.7 ^a	1.19	—	—	—	—

^a Minimum.

^b Drawn out wave

^c The compound is hydrolyzed.

^d Poorly defined wave which merges with the hydrogen wave.

Crotonaldoxime exists in a higher melting and a lower melting form. The higher melting isomer, which is investigated here, shows resemblance with the *anti* cinnamaldoxime and the *anti* benzaldoxime in the behaviour in alkaline solution, where the higher melting form of crotonaldoxime and the mentioned *anti* oximes gives rise to a reduction wave due to the reduction of the unprotonated oxime of nearly the same height as that in acid solution, whereas the *syn* isomers give a smaller wave.

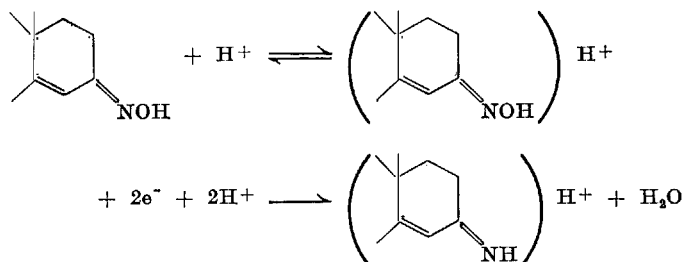
The polarographic wave of mesityloxi-oxime is like the first wave of crotonaldoxime apart from a slight tendency to forming minimum. No wave appears in alkaline solution. The wave in acid solution was shown to be due to a four electron reduction.

Carvone oxime produces in mineral acid solution two two-electron waves which about pH 2 merge into one four-electron wave. This wave disappears

at higher pH-values and pronounced minima are found in this pH-interval. No reduction takes place in alkaline solution.

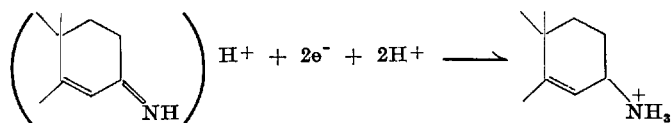
Testosterone propionate oxime is reduced in two two-electron reductions in acid solution until pH about 6, where the waves become deformed and diminish in height. The oxime is rather stable in acid solution at room temperature as the height of the waves at pH 1.0 is not diminished to any measurable degree during a period of 40 h.

Controlled potential reduction at pH 1 at -0.90 V vs S.C.E., which is the plateau of the first wave, showed that this wave was due to a two electron reduction. From the reaction mixture testosterone propionate could be isolated in good yield. The possibility that the oxime was hydrolyzed and the hydroxylammonium ion reduced must be excluded, as hydroxylamine is not reduced at that potential and the oxime was found to be stable at room temperature at pH 1. The reaction can thus be formulated:



followed by hydrolysis of the ketimine.

From controlled potential reduction at pH 1 at -1.2 V vs S.C.E., which is the plateau of the second wave, it was found that the total reduction of the oxime consumed four electrons and the second one thus two electrons. From this reduction was isolated an amine and the electrode reaction of the second wave, therefore, probably is the reduction of the formed ketimine to the amine:



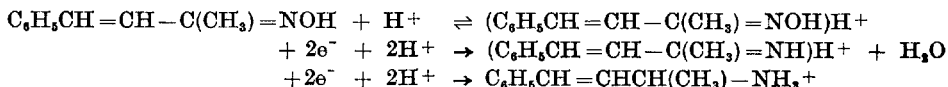
The *anti* cinnamaldoxime shows a single pH-dependent wave at pH values lower than 6. At pH 1 the height of the wave varies with the height of the mercury reservoir as required for a diffusion controlled wave. About pH 6 the wave becomes drawn out and the wave diminishes somewhat. The height of the wave in strongly alkaline solution is, however, more than half of the height in acid solution. The height of the wave in strongly alkaline solution varies with the height of the mercury reservoir, but somewhat less than required for a diffusion controlled wave.

The *syn* cinnamaldoxime resembles the *anti* isomer in acid solution but is different from it in alkaline medium. In strongly alkaline solution the wave disappears almost.

Controlled potential reduction in acid solution yielded some saturated aldehyde and the main product was cinnamylamine. The reaction consumed 3.8 electrons per molecule. In alkaline solution the *anti* cinnamaldoxime was reduced in a four electron reduction and hydrocinnamaldehyde was isolated in good yield.

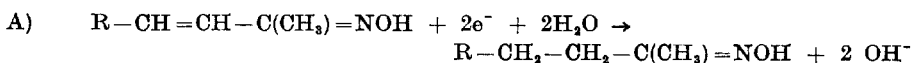
Benzalacetone oxime shows in strongly acid solution a single wave the height of which varies linearly with the square root of the height of the mercury reservoir. The half-wave potentials of this wave vary linearly with pH from pH 0 to pH 6. At pH-values higher than 3 a second, smaller wave is found whose nature was not investigated further. In strongly alkaline solution a single wave is found, the height of which is somewhat bigger than half of the wave height in strongly acid solution. The height of the wave at pH 13 varies somewhat with the height of the mercury reservoir, but not as much as required by a diffusion controlled wave.

From controlled potential reduction in mineral acid solution of benzalacetone oxime it was found that the reaction consumed 3.5 electrons per molecule. The main product, 1-methyl-3-phenyl-allylamine, was accompanied by some benzylacetone and another saturated ketone. In view of the results obtained for testosterone propionate oxime the reaction might be formulated:

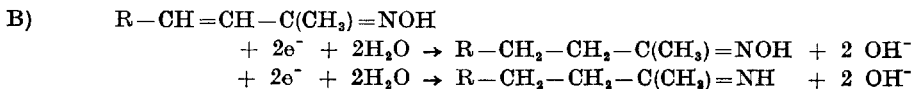


The formation of benzylacetone might be due to a reduction of the carbon-carbon double bond followed by hydrolysis of the benzylacetone oxime or to a reaction similar to that in alkaline solution.

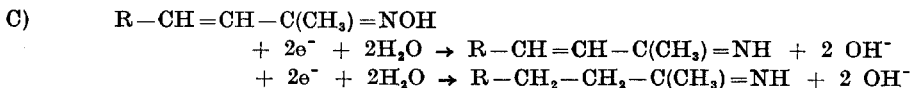
In alkaline solution the benzalacetone oxime was reduced in a four electron reduction and besides the main product, benzylacetone, a very small amount of amine could be isolated. The reaction might be formulated to proceed in at least three ways:



followed by alkaline hydrolysis of the oxime and a two electron reduction of the formed hydroxylamine.



followed by alkaline hydrolysis of the ketimine.



followed by hydrolysis of the ketimine to the ketone. It can not, however, be excluded that the hydrolysis precedes the last reduction which then would be the reduction of the benzalacetone to benzylacetone.

The first formulation is unlikely on the following grounds. Hydroxylamine is not reducible at the potential used in alkaline solution. Furthermore, benzylacetone oxime is not hydrolyzed easily in alkaline solution, which was shown by leaving a 10^{-3} M solution of benzylacetone oxime in 0.1 N sodium hydroxide for 18 h. The concentration of the oxime did not diminish to any appreciable degree which was found by polarography of the solution after lowering the pH to 3.

The second formulation (B) is unlikely, as benzylacetone oxime is not reduced in alkaline solution. No evidence has been found against the third formulation (C), why it must be regarded as the most likely approximation to the reaction path.

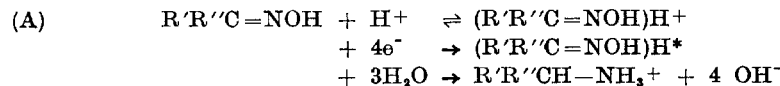
Aromatic oximes. The polarographic behaviour of oximes of simple aromatic carbonyl compounds have been thoroughly investigated elsewhere. Here the *syn* and *anti* benzaldoxime, which only seem to have been investigated in unbuffered systems^{15,16}, and oximes of some aminocarbonyl compounds have been included in the investigation.

The oximes of the aminocarbonyl compounds show a similar behaviour as, e.g., acetophenone oxime and the electrode reaction was shown to be a four electron reduction to the amine.

The *syn* and *anti* benzaldoxime are very much alike in their polarographic behaviour below pH about 4, whereas at higher pH-values they behave differently from each other. The *syn* benzaldoxime produces in weakly alkaline solution only a small wave, whereas the reduction wave due to the reduction of the unprotonated oxime of the *anti* benzaldoxime is nearly as high as in weakly acid solution. In strongly alkaline medium the height of the wave of the *anti* benzaldoxime diminishes somewhat, probably due to the formation of the anion $R-CH=NO^-$.

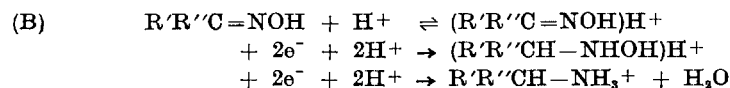
Controlled potential reduction of benzophenone oxime at pH 3 yielded benzhydramine in a four electron reduction. *Anti* benzaldoxime was reduced at pH 9, where the unprotonated oxime is reduced, in a four electron reduction and benzylamine was the isolated product.

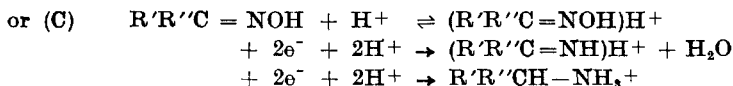
The reduction of aromatic oximes has been formulated¹⁰ in the following way:



where the symbol * represents an activation state or series of such states the charge type being unspecified.

An alternative formulation with two consecutive reductions occurring at the same potential (or at different potentials as in the cases of benzophenone oxime in strongly acid solution¹⁰), which evades the assumption of an electron uptake in aqueous solution of four electrons before an uptake of hydrogen ions, would be:





Of these (B) is unlikely as benzyldihydroxylamine is not reduced in mineral acid solution (Table 2) and in slightly acid solution the reduction occurs at a potential appreciably more negative than the half-wave potential of benzaldoxime. Although the intermediate aldimine (C) is too unstable in acid solution to be investigated polarographically it seems not unlikely that the electron uptake is a faster reaction than the hydrolysis. In this connection it can be mentioned that benzyldiene-methylamine in cold 50 % sulfuric acid has been reduced at a lead cathode in a two electron reduction to benzylmethylamine¹⁷. Although the postulated aldimine probably exists as an activated complex at the electrode surface it is believed that (C) gives a better approximation to the reaction path than (A) or (B).

N-benzylbenzaldoxime. The polarographic behaviour of this compound resembles somewhat that of *anti* benzaldoxime (Table 3). In strongly acid solution, however, where the compound is hydrolyzed too rapidly for exact polarographic measurements, two waves are found, which merge into one wave about pH 3. About pH 8 the wave splits in two waves, but in more alkaline solution again one wave is found with a height somewhat lower than in weakly acidic solution.

Controlled potential reduction in neutral solution showed that the main reaction was a four electron reduction of the *N*-benzylbenzaldoxime to dibenzylamine. In mineral acid solution, where two waves are observed, the first wave is apparently not corresponding to the reduction of the carbon-nitrogen double bond, as the expected product from such a reduction, dibenzylhydroxylamine, is not reducible in acid solution at the potential used. The reaction path in acid solution and probably also in neutral medium would thus be:

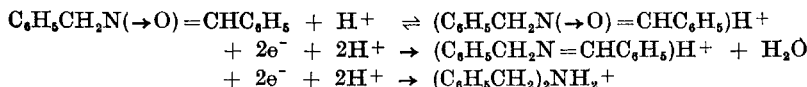


Table 3. Limiting currents in μA and half-wave potentials *vs* S.C.E. of *N*-benzylbenzaldoxime, *N,N*-dibenzylhydroxylamine, mesoxalic acid ester oxime, and benzamideoxime. Concentration 10^{-3} M. 0.01 % gelatine added as maximum suppressor.

pH	1.05		3.55		5.20		7.40		9.80		13	
Compound	i_d	$-E_{\frac{1}{2}}$	i_d	$-E_{\frac{1}{2}}$	i_d	$-E_{\frac{1}{2}}$	i_d	$-E_{\frac{1}{2}}$	i_d	$-E_{\frac{1}{2}}$	i_d	$-E_{\frac{1}{2}}$
<i>N</i> -Benzylbenzaldoxime	a	0.51	7.5	0.86	8.5	0.97	8.0	1.08	7.6 ^b	1.40	5.1	1.57
<i>N,N</i> -Dibenzylhydroxylamine	a	0.71	4.8 ^b	1.29	1.8	1.38	—	—	—	—	—	—
Mesoxalic acid ester oxime		9.3	0.85	9.1	1.02	9.1	1.05	8.9	1.07	8.6	1.31	—
Benzamideoxime	—		4.3	1.32	4.5	1.36	2.9	1.51	1.2	1.71	—	5.1 ^a 1.55

^a The compound is hydrolyzed.

^b drawn out wave.

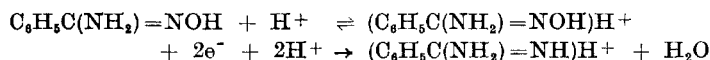
From a controlled potential oxidation at a mercury anode at -0.05 V vs S.C.E. in alkaline solution of dibenzylhydroxylamine was isolated N-benzylbenzaldoxime and benzaldehyde.

Ethyl ester of mesoxalic acid oxime. This compound has previously been investigated by Souchay and Ser⁹ and the results obtained here are substantially in agreement with theirs. The half-wave potentials found in the medium used here are, however, somewhat more negative and the height of the wave corresponds nearly to a four electron reduction. The polarographic behaviour of the ester resembles that of oximes containing two keto groups in the α -positions to the oxime group⁹ and also that of N-benzylbenzaldoxime.

From the height of the wave of mesoxalic acid oxime Sartori *et al.*¹⁸ concluded that the electrode reaction was a two electron reduction to the hydroxylamino malonic acid. Controlled potential reduction at pH 6 to the ester showed, however, that the electrode reaction in this case was a four electron reduction and aminomalonic acid ester was isolated from the reaction mixture. The electrode reaction is thus similar to that of other oximes.

Benzamideoxime. The polarographic behaviour of this compound resembles somewhat that of the unconjugated oximes. In strongly acid solution the wave is masked by the hydrogen wave but from pH about 2 a single wave is found. The height of this wave diminishes from pH about 6 and the wave disappears completely about pH 10. No minima has been observed in weakly alkaline solution. The height of the wave at pH 3 to 5 corresponds to a two electron reduction, whereas ordinary oximes are reduced by a four electron reduction.

Controlled potential reduction in aqueous solution at pH 4.8 of benzamideoxime confirmed that the electrode reaction consumed two electrons per molecule, and benzamidine, $C_6H_5C(NH_2) = NH$, was isolated in good yield as the picrate.



This reaction is similar to that postulated above as the first step of the reduction of ordinary oximes.

Benzalazine

Benzalazine has previously been investigated⁶ in 70 % ethanol containing 0.5 M tetramethylammonium chloride. The results obtained in 40 % ethanol containing 1 M potassium chloride are somewhat different from those reported and are given in Table 4. The results of the polarographic investigation of benzaldehyde benzylhydrazone in the same medium are included in the table.

The benzalazine, which is rapidly hydrolyzed in mineral acid solution, shows a single pH-dependent wave at pH values lower than 7. Between 6 and 9 the height of the wave diminishes rapidly and shows a pronounced minimum. The height of the first wave is determined by the rate of some reaction which might be the recombination of the benzalazine and H^+ to the easier reducible protonated benzalazine or might rather be some reaction involving the primarily formed reaction product. The first wave degenerates to another pH-

Table 4. Limiting currents in μA and half-wave potentials vs S.C.E. at different pH-values of benzalazine and benzaldehyde benzylhydrazone. Concentration 10^{-3} M. 0.01 % gelatine added as maximum suppressor.

pH	1.05		3.55		5.20		7.40		9.80		13		
	i_d	$-E_{\frac{1}{2}}$	i_d	$-E_{\frac{1}{2}}$	i_d	$-E_{\frac{1}{2}}$	i_d	$-E_{\frac{1}{2}}$	i_d	$-E_{\frac{1}{2}}$	i_d	$-E_{\frac{1}{2}}$	
Benzalazine	^a 0.73	14.7	0.91	15.2	1.05	13.1 ^b	1.15	4.5	1.24	0.9	1.49	5.9	1.46
Benzaldehyde-benzylhydrazone	4.6	0.56	9.2	0.85	8.7	1.03	7.3 ^b	1.19					

^a The compound is hydrolyzed.

^b Minimum.

dependent wave with a smaller wave height. This wave splits up in two waves in the pH-region 9.5—12. The wave with the most negative half-wave potential grows at the sacrifice of the other one in a manner, which resembles the reduction of *e.g.*, pyruvic acid.

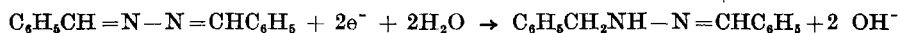
The height of the wave about pH 4 is between 2.5 and 3 times the height of the wave in alkaline solution, where the wave is diffusion controlled. The height of the wave in alkaline solution corresponds to a two electron reduction, and a reduction requiring 5 to 6 electrons would then be expected in acid solution.

Benzaldehyde benzylhydrazone shows at about pH 1 two waves of equal height which merge to one wave about pH 3. Between pH 6 and 9 the height of the wave diminishes rapidly and disappears completely about pH 9. The height of the wave about pH 4 is between 1.5 and 2 times higher than the height of the wave of benzalazine in alkaline solution, and a reduction requiring 3 to 4 electrons per molecule would, therefore, be expected.

On comparing the half-wave potentials of benzalazine and benzaldehyde benzylhydrazone it is found that the half-wave potentials of the latter is equal to or less negative than the half-wave potentials of benzalazine, and in a mixture of the two compounds the benzaldehyde benzylhydrazone would thus be reduced before or simultaneously with benzalazine.

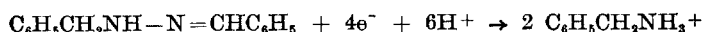
The polarographic behaviour of benzalazine could, therefore, be explained by assuming that the first wave was due to a reduction of benzalazine to benzaldehyde benzylhydrazone followed immediately by a reduction of this compound. If a two electron reduction wave is subtracted from the polarograms of benzalazine the resulting polarograms are very much like those of benzaldehyde benzylhydrazone.

Controlled potential reduction of benzalazine in alkaline solution showed that the electrode reaction consumed two electrons per molecule, and the isolated product was benzaldehyde benzylhydrazone

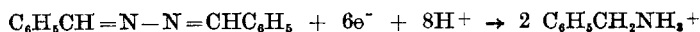


Dibenzyl diimide, $C_6H_5CH_2-N=N-CH_2C_6H_5$ ⁶, has been suggested as the reduction product, but this compound is known to rearrange to benzaldehyde benzylhydrazone under the influence of alkali or acid. It cannot, however, be excluded that dibenzyl diimide is the primarily formed product, although in view of the reducibility of azobenzene it would not seem unlikely that dibenzyl diimide would be reduced further to dibenzylhydrazine.

At pH 5 benzaldehyde benzylhydrazone was reduced in a four electron reduction, and benzylamine was isolated from the reaction mixture. The reaction path is probably similar to that of benzaldehyde phenylhydrazone to be discussed later.



In weakly acid solution benzalazine was reduced consuming 5.5 electrons per molecule and benzylamine was isolated from the reaction. The main reaction is:



Phenylhydrazones

α,β -Unsaturated phenylhydrazones. Carvone phenylhydrazone produces in mineral acid solution two waves of equal height which merge into one wave about pH 3. This wave diminishes in height from pH about 5 and disappears completely about pH 8. Controlled potential reduction at pH 4 showed that the electrode reaction consumed four electrons per molecule and aniline was isolated from the reaction mixture indicating a reductive splitting of the nitrogen-nitrogen bond.

Aromatic phenylhydrazones. The phenylhydrazones of the following aromatic carbonyl compounds were investigated: benzaldehyde, benzophenone, N-*p*-dimethylamino benzaldehyde, and *p*-aminoacetophenone. As seen from Table 5 they all show a single, pH-dependent wave in acid solution, which diminishes in height at higher pH-values and disappears completely in alkaline solution. The half-wave potentials of the hydrazones were from 0.05 to 0.2 V more positive than those of the carbonyl compounds. In the table are included the data of N-benzyl-N'-phenyl-hydrazine.

In the pH-region where the wave height is approximately constant the half-wave potentials have a nearly linear dependence of pH. For the amino-compounds the influence of the amino group makes the pH-dependence more complicated in neutral solution. In alkaline medium are found pronounced minima as for the oximes. The explanation of these minima and the diminishing of the wave height at higher pH-values is probably the same as for the oximes ⁹.

Controlled potential reductions of benzaldehyde phenylhydrazone, benzophenone phenylhydrazone, and N-*p*-dimethylamino benzaldehyde phenylhydrazone in acid solution showed that the electrode reaction consumed four electrons per molecule and that the overall reaction could be formulated as follows:

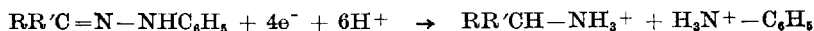


Table 5. Limiting currents in μA and half-wave potentials vs S.C.E. of some phenylhydrazones and N-benzyl-N'-phenylhydrazine at different pH-values. Concentration 10^{-3} M. 0.01 % gelatine added as maximum suppressor.

pH	1.05		3.55		5.20		7.40		9.80		13	
	i_d	$-E_{\frac{1}{2}}$	i_d	$-E_{\frac{1}{2}}$	i_d	$-E_{\frac{1}{2}}$	i_d	$-E_{\frac{1}{2}}$	i_d	$-E_{\frac{1}{2}}$	i_d	$-E_{\frac{1}{2}}$
Benzaldehyde	10.2	0.75	11.4	1.00	11.0	1.11	1.4	1.24	—	—	—	—
<i>p</i> -Dimethyl-aminobenzaldehyde	8.8	0.73	8.8	0.94	8.8	1.08	7.6 ^a	1.27	—	—	—	—
<i>p</i> -Aminoacetophenone	6.7	0.87	7.9	1.08	7.9	1.21	5.9 ^a	1.38	—	—	—	—
Cinnamaldehyde	10.5	0.72	9.8	1.00	8.1 ^a	1.12	4.3 ^a	1.21	0.7	1.32	—	—
Carvone	5.0	0.78	9.1	1.09	8.5	1.20	2.6 ^a	1.39	4 ^b	1.75	4 ^b	1.75
	4.7	1.06	—	—	4.1 ^a	1.44	—	—	—	—	—	—
N-Benzyl-N'-phenylhydrazine	—	—	—	—	—	—	-5	0.13	-3.8	0.38	-3.6	0.61

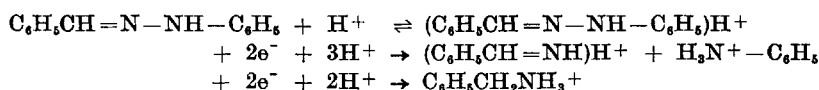
^a Minimum.

^b Merge with the sodium wave.

The same results were obtained by Tafel and Pfeffermann¹⁹ from the reduction of the phenylhydrazones of acetaldehyde, acetone, and benzaldehyde in 50 % sulfuric acid at a lead cathode. In the last case a small amount of benzylaniline was isolated besides the benzylamine and aniline.

The reduction of benzaldehyde phenylhydrazone might proceed by a reduction to N-benzyl-N'-phenylhydrazine followed by a reductive splitting of the nitrogen-nitrogen bond or a disproportionating to the amines and the hydrazone. This seems, however, unlikely as N-benzyl-N'-phenyl hydrazine is not reducible at the dropping mercury electrode and the compound seems perfectly stable in acid solution.

The cleavage of the protonated nitrogen-nitrogen bond seems, therefore, to be the initial step in the reaction and this is followed by a reduction of the formed aldimine:



The side reaction, which occurs in 50 % sulfuric acid and leads to the formation of benzylaniline, is also better explained on the assumption that benzaldimine is the intermediate product than if the reduction of the carbon-nitrogen double bond is assumed to be the initial step.

A reductive cleavage of a nitrogen-nitrogen bond has previously been reported for the reduction of 3-hydroxy-1,3-diphenyl-triazene, which in a four electron reduction followed by a two electron reduction forms aniline and phenylhydrazine²⁰.

Semicarbazones

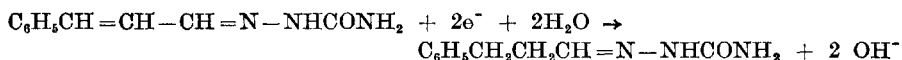
α,β -Unsaturated semicarbazones. Cinnamaldehyde semicarbazone produces in acid solution a single wave the height of which diminishes at higher pH-values and disappears about pH 10. From pH about 8 another wave appears, which is found in both weakly and strongly alkaline solution. The half-wave potentials of the first wave is pH-dependent, whereas the second one is not. The height of the first wave is determined by the rate of the recombination of the semicarbazone and the hydrogen ion, whereas the second one is diffusion controlled. This second wave is due to the reduction of the unprotonated semicarbazone.

Table 6. Limiting currents in μA and half-wave potentials vs S.C.E. of some semicarbazones at different pH-values. Concentration 10^{-3} M. 0.01 % gelatine added as maximum suppressor.

pH	1.05		3.55		5.20		7.40		9.80		13	
	i_d	$-E_{\frac{1}{2}}$	i_d	$-E_{\frac{1}{2}}$	i_d	$-E_{\frac{1}{2}}$	i_d	$-E_{\frac{1}{2}}$	i_d	$-E_{\frac{1}{2}}$	i_d	$-E_{\frac{1}{2}}$
Semicarbazone of												
Citral	9.4	0.87	9.7	1.08	8.0	1.24	2.1	1.40	—	—	—	—
Cinnamaldehyde	8.6	0.73	5.0	0.94	4.7	1.10	3.6	1.22	0.5	1.29	—	—
Benzalacetone	6.4	0.77	3.5	0.93	2.8	1.02	4.0	1.21	1.4*	1.27	—	—
Benzaldehyde	3.4	1.16	8.6	1.24	6.0	1.32	—	—	3.3	1.65	4.0	1.65
<i>p</i> -Aminoacetophenone	10.3	0.80	9.1	1.08	4.7*	1.20	—	—	—	—	—	—
	4.1	0.90	6.9	1.11	6.4*	1.24	3.8*	1.39	—	—	—	—
	1.9	1.03										

* Minimum.

Controlled potential reduction of cinnamaldehyde semicarbazone in alkaline solution showed that the electrode reaction consumed two electrons and the isolated product was hydrocinnamaldehyde semicarbazone:

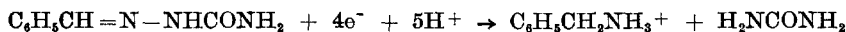


Attempts to reduce cinnamaldehyde semicarbazone in mineral acid solution was unsuccessful due to a partial hydrolysis of the semicarbazone.

Benzalacetone semicarbazone shows a similar behaviour as cinnamaldehyde semicarbazone. The benzalacetone semicarbazone is hydrolyzed in mineral acid solution, whereas it is stable in alkaline solution. Controlled potential reduction in alkaline medium showed that the electrode reaction was a two electron reduction to benzylacetone semicarbazone.

Aromatic semicarbazones. The semicarbazones of benzaldehyde and *p*-aminoacetophenone were investigated. Both showed a single pH-dependent wave in acid solution and the wave height diminished at higher pH-values. No wave was observed in alkaline solution. As in the cases of phenylhydrazones and oximes the semicarbazones showed pronounced minima in neutral and weakly alkaline solution.

Controlled potential reduction in mineral solution showed that a reductive splitting of the nitrogen-nitrogen bond took place in a reaction consuming four electrons per molecule. For benzaldehyde semicarbazone the overall electrode reaction thus is:

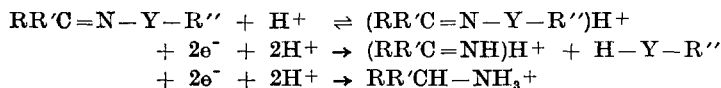


The reduction path is probably similar to the that of the reduction of benzaldehyde phenylhydrazone.

From the reduction of benzophenone semicarbazone, for which Souchay and Graizon ⁷ from the height of the polarographic wave suggested a 2 electron reduction to 1-benzhydryl semicarbazide, benzhydrylamine was obtained in good yield (70 %) in mineral acid solution. In an acetate buffer, pH 4, however, the reduction required less than 4 electrons and 1-benzhydryl semicarbazide was isolated in 30 % yield.

DISCUSSION

From the data presented it appears that in the polarographic reduction of $\text{RR}'\text{C}=\text{NYR}''$ the reaction depends on the nature of Y. Is Y a carbon atom, then the reduction consumes two electrons per molecule and the saturated compound is the reaction product. When, however, Y is nitrogen or oxygen the most common overall reaction in acid solution consumes four electrons per molecule and a reductive splitting of the N—Y bond takes place together with a saturation of the double bond. It also appears, that in general the splitting of the N—Y bond precedes the reduction of the carbon-nitrogen double bond thus giving the following reaction path:



In a few cases, *e.g.* benzophenone semicarbazone at pH 4, however, the four electron reduction is accompanied by a two electron reduction of the carbon-nitrogen double bond and the compound formed by this two electron reduction is not reduced further. This might also be the case in the reduction of dimethylglycylhydrazones of α,β -unsaturated steroid ketones ⁵, where the wave height of the hydrazones were found to be twice the wave height of the uncondensated steroid ketones. As α,β -unsaturated steroid ketones are reduced by a one electron reduction ²¹, this would suggest a two electron reduction of the hydrazones. However, no controlled potential reduction of the dimethylglycylhydrazones were made due to their low stability in acid solution, and the nature of the electrode reaction is, therefore, still uncertain.

EXPERIMENTAL

The polarograph was a recording polarograph Radiometer Type PO 3a. The capillary delivered 2.27 mg of mercury per second at a corrected mercury column height of 48.5 cm. The drop time 3.90 sec. (H_2O , open circuit). The capillary constant $m^{2/3}t^{1/6} = 2.17 \text{ mg}^{2/3}\text{sec}^{-1/6}$.

The apparatus used for the controlled potential reductions was an electromechanical potentiostat of the Lingane-Jones type. For the oxidations performed at an anode potential of -0.05 to -0.5 V vs S.C.E. the manually operated apparatus employed in Part I²¹ was found suitable.

The buffer solutions used were from pH 2.5 to 8 a sodium phosphate-citric acid buffer and from pH 8 to 11 a sodium borate buffer. The medium employed was 40 % alcohol containing 1 M potassium chloride and 0.01 % gelatine.

The carbonyl derivatives were prepared in the conventional way. The only derivative whose data apparently not have been reported previously is testosterone propionate oxime, which was prepared from 5 g of testosterone propionate, 5 g of hydroxylamine hydrochloride and 4 ml pyridine in methanol solution. After 3 days at room temperature the mixture was diluted with water and the precipitate recrystallized from dilute alcohol and benzene-hexane. M. p. 184° . $(\alpha)_D = +132^\circ$ (1 % in CHCl_3).

Reduction of cyclohexanone in methylamine solution. 1.0 ml of freshly redistilled cyclohexanone was reduced in a mixture of 40 ml 33 % aqueous methylamine solution, 50 ml 4 N hydrochloric acid, and 100 ml water at -1.65 V vs S.C.E. After completion of the reduction which required 2 electrons per molecule cyclohexanone the reaction mixture was extracted three times with ether, which was washed three times with dilute sodium hydroxide. After drying, the ether was evaporated, together with the remaining traces of methylamine. The residue was dissolved in ether and on addition of dry hydrogen chloride a precipitate, 925 mg, was obtained, which after recrystallization from alcohol-ether had m. p. $175-176^\circ$. It was identified as N-methyl cyclohexylamine hydrochloride (m. p.²² $175-178^\circ$). (Found: C 55.95; H 10.76; N 8.90; Cl 23.56. Calc. for $\text{C}_7\text{H}_{16}\text{NCl}$: C 56.16; H 10.79; N 9.36; Cl 23.70.)

Reduction of benzophenone anile. 1.0 g of benzophenone anile was reduced in a medium of 40 % peroxide free tetrahydrofurane, 20 % alcohol and 40 % water. The buffer was a borate buffer pH 10, the cathode potential -1.70 V vs S.C.E. Small amounts of acid were added during the reduction to compensate for the hydrogen ions used; the consumption of hydrogen ions was calculated from the reading of the coulometer. — The yellow colour of the solution disappeared during the reduction, which required two electrons per molecule. After completion of the reaction the mixture was diluted with water, made a little more alkaline and extracted three times with ether. The combined extracts were dried with potassium carbonate, and on addition of dry hydrogen chloride a precipitate, 1.05 g, was obtained, m. p. 203° , which was identified as benzhydryl aniline hydrochloride, m.p.²³ $201-203^\circ$. (Found: C 76.98; H 6.12; N 4.90; Cl 11.54. Calc. for $\text{C}_{19}\text{H}_{18}\text{NCl}$: C 77.16; H 6.13; N 4.74; Cl 11.97.)

Reduction of testosterone propionate oxime (1). A solution of 0.5 g testosterone propionate oxime was reduced in 180 ml 50 % alcohol containing 0.5 N HCl at -0.90 V vs S.C.E. until the first wave disappeared on the polarograms, which required 2.1 electrons. The reaction mixture was then extracted with chloroform, which was evaporated. The residue was dissolved in alcohol and added to an acid alcoholic solution of 2,4-dinitrophenylhydrazine. A precipitate, 0.7 g, was obtained, m. p. $190-195^\circ$; it was recrystallized from butanol and tetrahydrofurane-alcohol, m. p. $212-215^\circ$ after sintering about 210° . (Testosterone propionate 2,4-dinitrophenylhydrazone m. p. $209.9-210.5^{24}$, $217-218^{25}$). The IR-spectrum of the obtained hydrazone was found to be identical with that of actual testosterone propionate 2,4-dinitrophenylhydrazone.

Reduction of testosterone propionate oxime (2). A solution of 0.5 g of testosterone propionate oxime was reduced in 180 ml 50 % alcohol containing 0.5 N HCl at -1.20 V vs S.C.E. In this case a motor driven stirrer was found more suitable than a magnetic stirrer due to the formation of a surface-active reaction product. At higher concentrations of this compound the mercury emulgated thus making a further use of the electrode impossible. The reduction required a little less than four electrons. The reaction mixture was diluted with water, extracted with ether, made alkaline and again extracted with ether, which was dried. On addition of dry hydrogen chloride a precipitate, 275 mg, was obtained, m. p. $235-240^\circ$ (decomp.). The amine hydrochloride was rather slightly soluble in water. The amine was set free with carbonate and extracted with ether, which was evaporated. The amine had m. p. $218-222^\circ$. (Found: C 75.73; H 10.16; N 4.13. Calc. for $\text{C}_{22}\text{H}_{35}\text{NO}_2$: C 76.49; H 10.21; N 4.06.)

Reduction of anti cinnamaloxime (1). 1.0 g of anti cinnamaloxime was reduced in a mixture of 80 ml N H_2SO_4 , 80 ml alcohol, and 20 g of Na_2SO_4 at -0.8 V vs S.C.E. The

reduction consumed 3.8 electrons. After completion of the reduction the reaction mixture was extracted with ether, which was dried and evaporated leaving 225 mg of a compound with an IR-spectrum indicating the presence of an unconjugated aldehyde group. The aqueous phase was then made alkaline and extracted with ether, which was dried. On addition of dry hydrogen chloride a precipitate, 525 mg, was obtained, which was identified as cinnamyl amine hydrochloride through the benzoyl derivative, m. p. 93–94° (94–95°). (Found: C 80.73; H 6.37; N 5.75. Calc. for $C_{16}H_{15}NO$: C 80.98; H 6.37; N 5.91.)

Reduction of anti cinnamaldoxime (2). 1.0 g of *anti* cinnamaldoxime was reduced in 150 ml aqueous alkaline solution, to which benzene was added to dissolve the reaction product. The reduction required 4 electrons per molecule. After completion of the reaction the layers were separated and the aqueous phase extracted with ether. The combined organic solvents were washed with aqueous acid, from which a small amount of amine could be isolated. The organic solvents were evaporated leaving 800 mg of a compound which was identified as hydrocinnamaldehyde through the 2,4-dinitrophenylhydrazone, m. p. 149–151°. (Hydrocinnamaldehyde 2,4-dinitrophenylhydrazone, m. p. 147²⁶.)

Reduction of benzalacetone oxime (1). A suspension of 1.0 g of benzalacetone oxime was reduced at pH about 0.2 in 50 % alcohol containing sulfuric acid and sodium sulfate at -0.85 V vs S.C.E. The reduction consumed 3.5 electrons. The reaction completed, the mixture was diluted with water and extracted several times with ether, which was evaporated. The IR-spectrum (in chloroform) of the residue indicated the presence of benzylacetone. The residue, however, also contained another unconjugated ketone forming a 2,4-dinitrophenylhydrazone with m. p. 30–40° higher than that of benzylacetone. The reaction medium was then made alkaline and extracted several times with ether. The ether was extracted with dilute hydrochloric acid, and the amine benzoylated in alkaline solution, yielding 825 mg benzoyl derivative. It was identified as N-(methyl-cinnamyl)-benzamide from its m. p. 135–137° (N-(methyl-cinnamyl)-benzamide m. p. 136–137°). (Found: C 81.06; H 6.78; N 5.77. Calc. for $C_{17}H_{17}NO$: C 81.30; H 6.82; N 5.58.)

Reduction of benzalacetone oxime (2). A solution of 1.0 g benzalacetone oxime was reduced in 150 ml aqueous sodium hydroxide containing potassium chloride. 40 ml benzene were added to extract the reduction product as soon as it was formed. The compound was reduced at -1.70 V vs S.C.E. and the reduction required 3.9 electrons. After separation of the layers, the aqueous layer was extracted with ether, and the organic phase washed with acid, from which a small amount of amine (75 mg) could be isolated. The organic solvents were evaporated leaving 820 mg of a compound with an IR-spectrum identical with that of benzylacetone. On reaction with 2,4-dinitrophenylhydrazine a precipitate, m. p. 126°, was obtained (benzylacetone 2,4-dinitrophenylhydrazone, m. p. 125–126.3°²⁷).

Reduction of anti benzaldoxime. 1.0 g of *anti* benzaldoxime was reduced at pH 9 in a mixture of 30 % peroxide free tetrahydrofuran and 70 % aqueous buffer at -1.7 V vs S.C.E. The reduction required 4.0 electrons per molecule. After completion of the reaction the mixture was extracted three times with ether, which was dried. On addition of dry hydrogen chloride a precipitate, 700 mg, was obtained which was identified as benzylamine hydrochloride through the benzoyl derivative, m. p. 104–6° (N-benzyl-benzamide, m. p. 105–7°). (Found: C 79.65; H 5.99; N 6.70. Calc. for $C_{14}H_{13}NO$: C 79.57; H 6.21; N 6.64.)

Reduction of N-benzyl benzaldoxime. 1.0 g of N-benzyl benzaldoxime was reduced in aqueous medium of pH 7 at -1.2 V vs S.C.E. The reduction required 3.8 electrons per molecule. After completion of the reduction the reaction mixture was extracted with ether which was dried. On addition of dry hydrogen chloride a precipitate, 740 mg, was obtained, which after recrystallization from alcohol had m. p. 257–258°. (Dibenzylamine hydrochloride, m. p. 256°.) (Found: C 71.75; H 6.96; N 5.99; Cl 14.90. Calc. for $C_{14}H_{13}NCl$: C 71.93; H 6.90; N 6.00; Cl 15.17.)

Reduction of mesoxalic acid ester oxime. 1.0 g of mesoxalic acid ester oxime was reduced in a sodium bicarbonate solution that was saturated with carbon dioxide during the reduction, which required four electrons. pH was then raised to 9 and the mixture extracted with ether and ethyl acetate, which was dried. After addition of alcoholic hydrogen chloride the organic solvents were evaporated *in vacuo* and the residue dissolved in a small amount of alcohol. On addition of ether a precipitate was obtained with m. p. 159°, which was identified as aminomalonic acid ethylester hydrochloride (m. p. 162°). (Found:

C 39.76; H 6.76; N 6.81; Cl 16.70. Calc. for $C_7H_{14}NClO_4$: C 39.72; H 6.67; N 6.61; Cl 16.75.)

Reduction of benzamide oxime. 1.0 g of benzamide oxime was reduced in aqueous acetate buffer pH 4.7 at -1.3 V vs S.C.E. The reduction required two electrons per molecule. After completion of the reduction picric acid was added and a precipitate, 2.1 g, was obtained, which after recrystallization from alcohol had m. p. 231–233°. It was identified as benzamidine picrate (m. p. 233°) by its m. p. and analysis. (Found: C 44.72; H 3.07; N 20.10. Calc. for $C_{13}H_{11}N_5O_7$: C 44.71; H 3.17; N 20.05.)

Reduction of benzalazine. A suspension of 2.0 g of benzalazine in alkaline 50 % ethanol was reduced at -1.60 V vs S.C.E. The yellow colour of the solution disappeared as the reduction proceeded, and a white compound crystallized out. After consumption of 2 electrons per molecule the reduction was finished and the crystalline compound filtered off, m. p. 68–70°. It was identified as benzaldehyde benzylhydrazone (m. p. 65°, 69–70°). This compound is known to be unstable in contact with air, and the compound was, therefore, further characterized by its picrate, m. p. 130° (130°). (Found: C 54.25; H 3.95; N 15.91. Calc. for $C_{20}H_{17}N_5O_7$: C 54.66; H 3.90; N 15.94.)

Reduction of benzaldehyde benzylhydrazone. 1.5 g benzalazine was reduced in alkaline solution as described above (2 electrons per molecule). pH was then lowered to 5 by addition of glacial acetic acid and the reduction product from the alkaline reduction, benzaldehyde benzylhydrazone, reduced at -1.2 V vs S.C.E. After completion of the reduction which required 4 electrons hydrochloric acid was added and most of the solution evaporated *in vacuo*. The residue was made alkaline and extracted with ether which was dried. On addition of gaseous hydrogen chloride a precipitate, 1.08 g, was obtained which was identified as benzylamine hydrochloride from the m. p. 250–254° (250–256°) and the m. p. 104–106° of the benzoyl derivative (N-benzyl benzamide, m. p. 105–107°).

Reduction of benzaldehyde phenylhydrazone. A suspension of 1.0 g of benzaldehyde phenylhydrazone in a mixture of 90 ml peroxide free dioxane, 50 ml alcohol, and 50 ml N HCl was reduced at -0.80 V vs S.C.E. The reduction was completed after the consumption of 4.2 electrons. The reaction mixture was evaporated to dryness *in vacuo* and the residue dissolved in buffer pH 5. This was extracted with ether, which was shown to contain an amine, that could be diazotized. The aqueous phase was made alkaline and extracted with ether, which was dried. On addition of alcoholic hydrogen chloride a precipitate was obtained, m. p. 253–255°, which was recrystallized from alcohol-ether. The compound was identified as benzylamine hydrochloride from its analysis: (Found: C 58.37; H 7.08; N 9.74; Cl 24.75. Calc. for $C_7H_{10}NCl$: C 58.54; H 7.02; N 9.76; Cl 24.68.)

Reduction of benzophenone phenylhydrazone. A suspension of 1.0 g of benzophenone phenylhydrazone was reduced at -0.75 V vs S.C.E. in a mixture of 80 ml peroxide free dioxane, 80 ml alcohol, and 40 ml 2 N HCl. After completion of the reduction, which consumed four electrons per molecule, the reaction mixture was diluted with water and extracted with ether. pH was raised to 4 and the aqueous layer extracted with ether. The aqueous phase was then made alkaline and extracted with ether. After drying of this ether extract a precipitate, 460 mg, was obtained on addition of hydrogen chloride. It sublimed about 280°. It was identified as benzhydramine hydrochloride from its analysis. (Found: C 71.04; H 6.59; N 6.28; Cl 16.15. Calc. for $C_{13}H_{14}NCl$: C 71.07; H 6.42; N 6.37; Cl 16.14.)

Reduction of p-dimethylaminobenzaldehyde phenylhydrazone. 1.0 g of N-dimethylaminobenzaldehyde phenylhydrazone was reduced at pH 0.5 in 50 % alcohol. The cathode potential was -0.8 V vs S.C.E. The reduction was completed after the consumption of four electrons per molecule, and pH was then adjusted to 5. The reaction medium was extracted with ether, made alkaline and extracted several times with ether. The ether was dried and on addition of dry hydrogen chloride a precipitate, 480 mg, was obtained, which was identified as N^4, N^4 -dimethyl-toluene-*a*,4-diamine dihydrochloride from its analysis. (Found: C 48.33; H 7.28; N 12.56; Cl 31.51. Calc. for $C_9H_{16}N_2Cl_2$: C 48.44; H 7.23; N 12.56; Cl 31.79.)

Reduction of cinnamaldehyde semicarbazone. 1.0 g of cinnamaldehyde semicarbazone was reduced in alkaline, 50 % alcoholic solution at a cathode potential of -1.70 V. After consumption of two electrons per molecule the reaction was completed and the reaction mixture diluted with water. It was extracted with ether which was evaporated. The residue was recrystallized from dilute alcohol and benzene. It was identified as hydro-

cinnamaldehyde semicarbazone from the m. p. 124–126° (127°), and its analysis. (Found: C 63.16; H 6.95; N 21.58. Calc. for $C_{10}H_{13}N_3O$: C 62.80; H 6.86; N 21.97.) On boiling with 2,4-dinitrophenylhydrazine in dilute alcohol a 2,4-dinitrophenylhydrazone, m. p. 149–151° was obtained (Hydrocinnamaldehyde 2,4-dinitrophenylhydrazone, m. p. 147°²⁶).

Reduction of benzalacetone semicarbazone. A suspension of 1.0 g of benzalacetone semicarbazone was reduced at pH 13 in 50 % alcohol at a cathode potential of –1.70 V. The reduction required 2 electrons per molecule. The reaction mixture was then diluted with water and extracted with ether, which was evaporated. The residue was recrystallized from benzene-petrol ether, 0.65 g, m. p. 112°. The m. p. was not raised by recrystallization from dilute alcohol, but on recrystallization from benzene and seeding with a crystal of actual benzylacetone semicarbazone the m. p. was raised to 141–142° (benzylacetone semicarbazone m. p. 142°). (Found: C 64.19; H 7.36; N 20.48. Calc. for $C_{11}H_{15}N_3O$: C 64.37; H 7.37; N 20.47.) On boiling with 2,4-dinitrophenylhydrazine in dilute alcohol a 2,4-dinitrophenylhydrazone, m. p. 125–26°, was obtained. (Benzylacetone 2,4-dinitrophenylhydrazone, 125–126,3°²⁷).

Reduction of benzaldehyde semicarbazone. A solution of 1.0 g of benzaldehyde semicarbazone was reduced in a mixture of 70 ml peroxide free dioxane, 70 ml alcohol and 50 ml N HCl at a cathode potential of –0.85 V vs S.C.E. The reduction required four electrons. After completion of the reaction the solvents were evaporated *in vacuo* and the residue dissolved in alkali, which was extracted with ether. After drying dry hydrogen chloride was added and a precipitate m. p. 252–255° was obtained. The amine was benzoylated yielding a derivative m. p. 104–106° (N-benzyl benzamide m. p. 105–107°). (Found: C 79.54; H 6.04; N 6.30. Calc. for $C_{14}H_{13}NO$: C 79.57; H 6.21; N 6.64.)

Reduction of benzophenone semicarbazone. 1.0 g of benzophenone semicarbazone was reduced in 200 ml 50 % ethanolic 0.5 N HCl containing 3 g of semicarbazide hydrochloride at –0.9 V vs S.C.E. The reduction required four electrons per molecule. The reaction medium was extracted with ether after completion of the reduction, and 0.1 g of an unidentified compound was isolated from the ether. The aqueous phase was made alkaline and extracted with ether, which was dried. On addition of alcoholic hydrogen chloride a precipitate, 620 mg, was obtained, which was identified as benzhydrylamine hydrochloride from its analysis. (Found: C 70.85; H 6.60; N 6.40; Cl 16.00. Calc. for $C_{13}H_{14}NCl$: C 71.07; H 6.42; N 6.37; Cl 16.14.)

From the reduction of benzophenone semicarbazone at pH 4 a hydrochloride was isolated, which on recrystallization from water yielded a compound, that was identified as 1-benzhydrylsemicarbazide from its m. p. 165° (164–165°) and analysis. (Found: C 69.43; H 6.32; N 17.59. Calc. for $C_{14}H_{15}N_3O$: C 69.68; H 6.27; N 17.42.)

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