ELECTROCHEMICAL REDUCTION OF 2,2'-DINITRODIPHENYLMETHANE AND 2,2'-DINITROBENZOPHENONE AT MERCURY ELECTRODES

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The last two compounds in a 5-membered series of aromatic dinitro compounds are reduced in a completely different manner at mercury electrodes. 2,2'-Dinitrodiphenylmethane (*I*) — in which a conjugation of both symmetrical moieties is ruled out — is electrolytically reduced in an eight-electron step to a bishydroxylamine this being most stable between pH 4·5 and 5·0. In processing the catholyte increase in concentration of this product leads to its intermolecular disproportionation, resulting in the formation of dibenzo[*b*, *e*]-1,2-diazepine 5-oxide (*IV*) and 2,2'-diaminodiphenylmethane (*III*). 2,2'-Dinitrobenzophenone (*II*) reduces at more positive potentials. Its preparative electrolysis in acetonitrile (with 0·1M-$N(n\text{-}C_4H_9)_4PF_6$ as supporting electrolyte) the application of which was made necessary by the low solubility of *II* in ethanol, proceeds in an anomalous way. In the most positive cathodic wave a radical anion results, the following cathodic wave corresponds to a 6-electron reduction of one nitro group to an amino group while the other nitro group splits off as the anion NO_2^- (this later giving an anodic wave). Its formation has been proved by standard addition in polarography and by a qualitative analytical test. The product which results through this electrode process and a follow-up chemical reaction is acridone. This in turn, reduces in the third, most negative 4-electron wave to dihydroacridine.

The comparison of all substances studied in this series reveals that their reducibility decreases with respect to the link X, *viz.* in the sequence CO > O > S and CH_2 > NH. The electrolytical reduction on mercury cathodes occurs in a similar manner with analogues where X = O, S or CH_2. Here, the main intermediate is the bis-hydroxylamine the stability of which predetermines the structure of final products. The other group comprises the substances with X = CO and NH. Here the main intermediate is the 2-nitro-2'-amino-diphenyl-X which is formed in a 6-electron process taking place at one of the nitro groups. The follow-up cyclization reaction leading to seven-membered heterocyclic rings located between two benzene nuclei only occurs with analogues of the type X = CH_2, O and S. A partial reduction of dinitro compounds of this series has been observed with the analogue containing the NH link although that with X = CO has generally good preconditions for this mechanism.

In the preceding communications[1,2] the electrochemical behaviour at mercury cathodes of symmetrical compounds of the type 2,2'-dinitrodiphenyl — X was described where X was S, O and NH. The investigations were aimed in particular

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at follow-up cyclization reactions leading to the formation of a seven-membered heterocyclic ring with fused benzene nuclei. These reactions are induced by a partial reduction of both nitro groups. The series of investigations into this problem should be closed by this article where similar reactions are described as observed with 2,2'-dinitrodiphenylmethane (*I*) and with 2,2'-dinitrobenzophenone (*II*).

We intend to compare here the tendency of the individual members of the series to form seven-membered rings in cyclization reactions, further the differences in stability of intermediates containing hydroxylamine groups or, as the case may be, the possibility of reducing only one of both nitro groups. Finally, we are also going to formulate the influence of different structures of the starting material on the mechanism of the electrolytical reduction of nitro group and on the electrochemical properties of products.

2,2'-Dinitrobenzophenone (*II*) will probably reduce electrochemically in a more complicated manner than all other substances under investigation since, in addition to both nitro groups, it contains also the electroactive carbonyl group. On the other hand, the reduction of *I* should proceed quite simply because CH_2 as a link between the two aromatic parts ot the molecule excludes a transfer by conjugation of mesomeric effects.

The non-electrochemical reduction of *I* and *II* was studied with various reagents. After the reduction of *I* 2,2'-diaminodiphenylmethane[3,4,7], dibenzo(*b*, *e*)-(1,2)-diazepine[4,7] its reduced form[4,7] and its N-oxide[7] were identified among the products. The chemical reduction of the dinitro compound *II* yielded the following compounds: 2,2'-diaminobenzophenone[3], dibenzo-(*b*,*e*)-1,2-diazepin-11-one[5], 2,2'-dinitrodiphenylcarbinol[5], 2-methoxy-2'-nitrobenzophenone[5], 2,2'-diaminodiphenylcarbinol[5], 2-nitro-2'-aminobenzophenone[5]. Consequently, *II* makes possible the preparation of 2-nitro-2'-aminobenzophenone by partial chemical reduction.

EXPERIMENTAL

The techniques and instrumentation applied here were already described in our preceding communications[1,2]. dc-Polarographic measurements in acetonitrile with $N(n\text{-}C_4H_9)_4PF_6$ as supporting electrolyte, as well as cp-coulometry, were performed with a three electrode circuit making use of a saturated mercurous sulphate reference electrode. The shape of the *i*–*E*-curve containing no substance to be electrolysed was always checked before the electrolysis or before recording the dc-polarographic waves of these compounds and the coulometric measurements were corrected with respect to a blank. Acetonitrile, as well as ethanol, was only used after a careful rectification.

$N(n\text{-}C_4H_9)_4PF_6$ was recrystallized from ethanol. Analytical grade reagents were used for preparing the buffers, 2,2'-dinitrodiphenylmethane (*I*) and 2,2'-dinitrobenzophenone (*II*) were prepared according to procedure referred to in the preceding communication[8]. Dibenzo-(*b*,*e*)-1,2-diazepin-11-one was prepared as a model substance according to a procedure by Johns and Markham[5]. Following a sublimation and a recrystallization from ethanol orange needles resulted with m.p. 197·0–197·5°C (197°C is reported in the literature[5]).

For identifying the substances by IR spectra a UR 20 (Carl Zeiss, Jena) apparatus was used, the mass spectra were recorded with a Jeol MS 100 and elemental analysis was performed with the Elemental Analyser 1 104 Carlo Erba.

RESULTS AND DISCUSSION

DC-POLAROGRAPHY AND CYCLIC VOLTAMMETRY OF 2,2'-DINITRODIPHENYLMETHANE (*I*)

5 . 10^{-4} mol l^{-1} solutions of *I* with 50% (by vol.) ethanol yield two cathodic waves in the pH-region from 1 to 6·5; the ratio of their heights varies from 8 : 2 to 8 : 2·5. In neutral and alkaline solutions only a single cathodic wave results the height of which is almost the same as the height of the more positive wave in acid solutions. The $E_{1/2}$-pH-plot is shown in Fig. 1. The value of the slope $\Delta E_{1/2}/\Delta$ pH for the first wave of *I* is −0·085 V/pH up to pH 8·7. At pH-values exceeding 8·7 $E_{1/2}$ becomes pH-independent. The cathodic waves are irreversible, diffusion-controlled and exhibit a linear dependence on concentration of *I*.

Cyclic voltammetry (with a stationary mercury drop electrode) gives two cathodic peaks at −0·31 and −0·8 V (*vs* S.C.E.), respectively. At +0·17 V an anodic peak was observed which corresponds to an oxidation of the hydroxylamine intermediate *IIa* to a nitroso derivative. A cyclic voltammogram of *I* at pH 5·05 is shown in Fig. 2. Two cathodic peaks appear here at −0·63 V and −1·25 V, respectively. At −0·10 V the anodic peak corresponding to the oxidation of the hydroxylamine intermediate appears. A small, more negative anodic peak lies at −0·27 V. At pH 10·5 only one cathodic peak (E_p = −0·85 V) appears on the cyclic voltammogram (Fig. 3). Anodic peaks are formed here at −0·42 and −0·56 V (*vs* S.C.E.).

cp-Coulometric Measurements and Preparative Electrolysis

cp-Coulometric results obtained with *I* are summarized in Table I. Preparative electrolysis at pH 5 yields substance *IV* and 2,2'-diaminodiphenylmethane (*III*) as

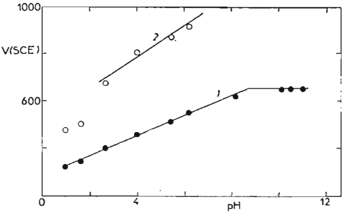


FIG. 1

$E_{1/2}$-pH plot for 5 . 10^{-4}M — *I* in solutions with 50% (by vol.) ethanol: *1* positive cathodic wave; 2 negative cathodic wave

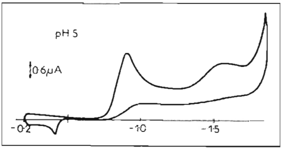


FIG. 2

Cyclic voltammogram of 5 . 10^{-4}M *I* at pH 5·0. Stationary mercury drop; scan rate 10 V min^{-1}, *vs* S.M.E main products if the reduction potential is adjusted to a value corresponding to the limiting current of the more positive cathodic wave. At the end of the electrolysis the catholyte exhibits a high anodic wave which reveals the presence of the hydroxylamine product *IIa* at a high concentration. This anodic wave increased during electrolysis in both acid and alkaline solutions and attained its maximum value in electrolyses at pH 4 – 5. With working potential set to a value corresponding to the limiting cur-

TABLE I

cp-Coulometric measurements at a large-area mercury electrode with 2,2'-dinitrodiphenylmethane (*I*) and 2,2'-dinitrodiphenylbenzophenone (*II*)

pH-value	Substance	Reduction potential V *vs* S.C.E.	n	$E_{1/2}$, V *vs* S.C.E. of the resulting anodic wave
1	*I*	−0·5^{a}	7·2	—
1	*I*	−0·9^{b}	8·5	—
1	*II*	−0·4^{a}	8·2	—
1	*II*	−0·8^{b}	15·0	—
5	*I*	−0·8^{a}	8·0	−0·07
5	*I*	−1·5^{b}	12·0	−0·07
5	*II*	−0·75^{a}	6·6	+0·04
5	*II*	−1·40^{b}	13·5	+0·04
10	*I*	−1·40^{a}	8·4	−0·40
10	*II*	−1·10^{a}	8·8	−0·30
10	*II*	−1·90^{b}	9·5	−0·30
10	*II*	−2·10^{c}	16·5	−0·30

[a] Corresponds to the limiting current of the first wave; [b] corresponds to the limiting current of the second wave; [c] corresponds to the limiting current of the third wave.

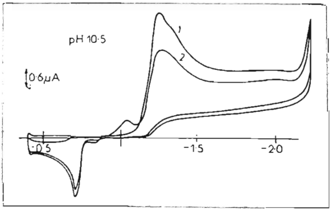


FIG. 3

Cyclic voltammogram of 5 . 10^{-4}M *I* at pH 10·0. Stationary mercury drop, scan rate 10 V min^{-1}, *vs* S.M.E; *1* first cycle, *2* second cycle rent of the more negative cathodic wave, the ratio of the diamine *III* in its mixture with *IV* increased. The main product isloated after electrolysis in alkaline solutions (at pH 10) was also the diazepin oxide *IV* with small quantities of the diamine *III*.

Products Isolated in Preparative Electrolysis

Dibenzo[b, e]-1,2-*diazepin* 5-*oxide* (IV). On extracting the catholyte with chloroform after electrolysis, the solvent was evaporated in a vacuum still and a substance resulted which, after recrystallization, had a m.p. 132°C (the literature[7] quotes a m.p. 130–132°C for diazepin oxide *IV*). The recording of the mass spectra yielded the corresponding M^+ 210 *m/e* and further fragments 194 *m/e*, 106 *m/e*, 104 *m/e*, 90 *m/e*.

Elemental analysis resulted in the following results: calculated for $C_{13}H_{10}N_2O$: 72·26% C, 4·80% H, 13·33% N; found: 72·37% C, 4·86% H, 13·16% N. The IR spectra measured in $CHCl_3$ had the following vibrational bands: 300 cm^{-1} (w), 1 490 cm^{-1} . . (w), 1 460 cm^{-1} (m), 1 420 cm^{-1} (s), 1 330 cm^{-1} (w), 1 300 cm^{-1} (w). The findings are in accordance with the diazepin oxide *IV*.

2,2'-*Diaminodiphenylmethane* (III). This compound was isolated from the mixture by chromatography on a poured silica gel column with a chloroform/ethanol system. The pure product had a m.p. 133°C (literature[5,7] quotes 134–136°C for $C_{13}H_{14}N_2$). Its elemental analysis led to following results: for $C_{13}H_{14}N_2$ calculated: 78·75% C, 7·12% H, 14·13% N; found: 78·61% C, 7·43% H, 13·55% N. The mass spectra yielded the corresponding M^+ 198 *m/e* and further fragments 182 *m/e*, 166 *m/e*, 106 *m/e*. All these data point to a correct ascription to the isolated compound of the diamine structure *III*.

TABLE II

Polarographic half-wave potentials of 2,2'-dinitrodiphenylmethane and its reduction products. Britton–Robinson buffer with 50% (by vol.) ethanol; pH 10·0

Substance	$-E_{1/2}$, V (S.M.E.)
I	0·91
IIa	0·40 (anodic)
III	irreducible
IV	0·92
VI	0·59
1,2-dihydrodibenzo-[*b*,*e*]-(1,2)-diazepine	0·59 (anodic)

Discussion on the Reduction of Substance I

The dinitro compound *I* reduces electrochemically to the bis-hydroxylamine *IIa* within the whole pH-region studied here. This fact is supported both by the high anodic waves resulting during preparative electrolysis and cp-coulometric micro-electrolysis and during cp-coulometry at large-area electrodes (Table I). At pH 4–5 the maximum height of the anodic wave is reached towards the end of the electrolysis and it amounts to one half of that of the more positive cathodic wave before electrolysis. A further electrolytical reduction of the nitro group takes place at more negative potentials only in the acid region up to pH 5·7. Regardless of the pains taken here even at optimum conditions of hydroxylamine stability in the solution, we did not succeed in isolating this substance from the solution. During the extraction and evaporation of the solvent in a vacuum evaporator, chemical follow-up reactions proceeded which give rise to new products. A TLC analysis of the residue on evaporating the solvent reveals that the product is a mixture, prevalently of substances *III* and *IV* which were actually identified.

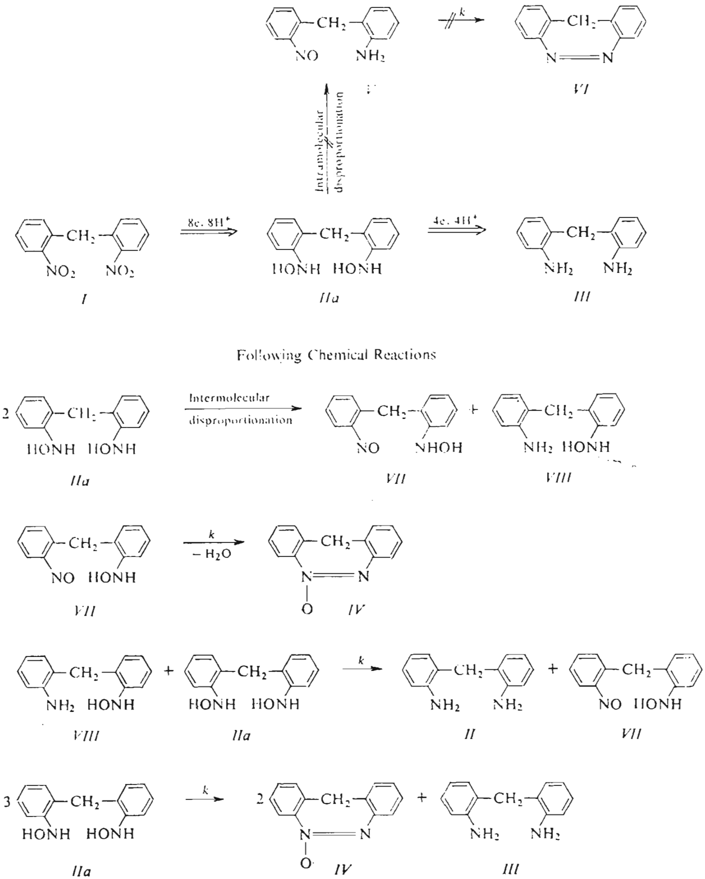
The formation of *IV* during processing the catholyte cannot be interpreted in terms of an intramolecular disproportionation of bis-hydroxylamine *IIa* to *V*; in a follow-up step the latter would react giving rise to the cyclic product *VI* which during the isolation would be oxidized to *IV*. However, substance *VI* is relatively resistent toward oxidation[4,7] and moreover, the above mechanism does not explain the presence of the diamine *III* in the reaction mixture, in particular in alkaline solutions where an electrode reduction of $—NO_2$ to NH_2 must be excluded.

If substance *IV* was already formed during electrolysis this would manifest itself in a decrease in height of the anodic wave of the resulting bis-hydroxylamine *IIa*. With respect to the value of its half-wave potential, substance *IV* would reduce first to the corresponding diazepine[8] *VI* and further to its dihydroform. This substance, however, has not been found and, moreover, substance *IV* is not formed by its oxidation (Scheme 1).

Basing on all these facts we assume that diazepinoxide *IV* is formed in an intermolecular disproportionation of the bis-hydroxylamine *IIa* to *IV* and diamine *III* which (Scheme 1) only results during the isolation of products when a higher concentration of *IIa* is secured. In accord with this, the products *IV* and *III* were isolated in an approximate ratio 2 : 1 from alkaline media.

DC-POLAROGRAPHIC AND VOLTAMMETRIC BEHAVIOUR OF 2,2′-DINITROBENZOPHENONE (*II*) IN WATER–ETHANOLIC SOLUTIONS

2,2′-Dinitrobenzophenone (*II*) was first studied in buffered solutions containing 50% (by vol.) ethanol. Over the pH-region from 1 to 10·5 two cathodic waves appear on the dc-polarogram. The more positive one exhibits a shape which points to a coalescence of two reduction steps. The more negative wave which probably corresponds to the reduction of the carbonyl group is also poorly developed. A quantitative



SCHEME 1

comparison of the ratio of their heights can be hardly made because of their difficult evaluability. In comparison with *I*, however, substance *II* reduces at more positive potentials. The results of coulometric measurements with *I* are shown in Table I. Both during microelectrolysis and preparative electrolysis an anodic wave is formed which probably corresponds to the oxidation of the bis-hydroxylamine intermediate. During the electrolysis its height attains a certain value which decreases again towards the end of electrolysis.

Cyclic voltammograms of *II* (Fig. 4 and 5) pointed also to a splitting of the more positive peak representing the electrolytic reduction of the nitro groups. The more negative cathodic peak corresponds then to the electrolytical reduction of the conjugated carbonyl group. In alkaline media a reversible cathodic peak corresponding to the formation of a radical anion appears on the cyclic voltammogram: this radical species is more stable in such a media. The anodic peak corresponding to the re-oxidation of the hydroxylamine intermediate can be virtually observed on all voltammetric curves regardless of the pH-value. A large-scale preparative electrolysis, however, could not be accomplished in water–ethanolic media because of the very poor solubility of the starting substance *II*. The attempts to perform preparative electrolysis at a lower concentration of *II* proceed very slowly and afford enough time for side reactions of intermediates to occur. This is why acetonitrile has been chosen as solvent for a thorough investigation of the electrochemical behaviour of *II*; N $(n\text{-}C_4H_9)_4PF_6$ served here as supporting electrolyte.

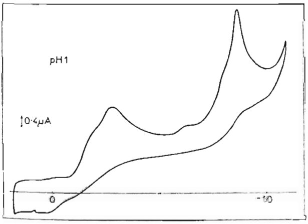


FIG. 4

Cyclic voltammogram of $5 \cdot 10^{-4}$M *II* at pH 1·0. Stationary mercury drop, scan rate 10 V min^{-1}, *vs* S.M.E

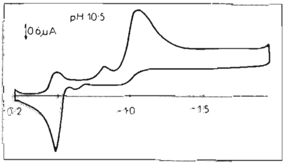


FIG. 5

Cyclic voltammogram of $5 \cdot 10^{-4}$M *II* at pH 10 5. Stationary mercury drop, scan rate 10 V min^{-1}, *vs* S.M.E

DC-POLAROGRAPHIC AND VOLTAMMETRIC BEHAVIOUR OF 2,2'-DINITROBENZOPHENONE (*II*) IN ACETONITRILE

dc-Polarographic curves recorded with anhydrous acetonitrile 0·1M-$N(n-C_4H_9)_4PF_6$ as supporting electrolyte yielded three cathodic waves with $E_{1/2} = -1·28$ V, $-1,53$ V and $-2·43$ V (all *vs* M.S.E.); the ratio of their heights is 7 : 38 : 80; all of them are diffusion-controlled and their heights are a linear function of concentration of *II*. The most positive, small wave is reversible as follows from the formation of an anodic wave with the same $E_{1/2}$ when using a Kalousek commutator (with discontinuously changed square wave voltage) or from cyclic voltammetry[13]. It corresponds to the formation of the radical anion of *II*. In Kalousek polarography, when setting E_{aux} in the producing period to a value corresponding to the limiting current of the second, more negative cathodic wave, a further, more positive, relatively high anodic wave forms on the commutated curve (its $E_{1/2}$ is $-0·94$ V). This wave probably represents an overlapping of the anodic wave of the hydroxylamine intermediate and of that corresponding to the oxidation of the split-off nitrite anions NO_2^-. The attempt to record a commutated wave with E_{aux} more negative than $-2·0$ V did not succeed because of disturbances on the dme (coverage of the surface by adsorbable and insoluble products). The addition of about 2·5% (by vol.) conc. acetic acid causes a single cathodic wave to appear with $E_{1/2} = -0·96$ V. The commutating in this media gave an anodic wave with $E_{1/2} = -0·37$ V.

cp-Coulometric Measurement

In cp-Coulometric electrolysis at the potential corresponding to the limiting current of the most positive cathodic wave, the starting substance *II* virtually does not change, the increase in the charge consumption is very slow. If, however, a potential in the region of the limiting current of the intermediate cathodic wave has been chosen, the colour of the catholyte turns orange and $n = 6$. As the only product of electrolysis, acridone (*XVII*) has been isolated. On the polarogram one can observe an anodic wave with $E_{1/2} = -0·44$ V, the decreased second (intermediate) wave and the unchanged last cathodic wave. On leading air through the solution the anodic wave does not change, but on adding several small crystals of $NaNO_2$ to this solution the anodic wave increase. (a standard solution of suitable concentration cannot be prepared in acetonitrile).

The presence of nitrite anions was also proved by quantitative analytical tests, either by Ilosvay reagent[8,9] or by an aqueous solution of *m*-phenylenediamine (Gries test)[9]. In comparison with a blank (catholyte before electrolysis) the catholyte after electrolysis, exhibiting the anodic wave, gave a positive test with both reagents. From all this the following conclusion can be made: at the potential of the second cathodic wave not only a six-electron reduction of a single nitro group occurs but, moreover, the second nitro group splits off in a chemical follow-up reaction as NO_2^-. From the intermediate thus formed acridone (*XVII*) results in a chemical follow-up reaction.

In cp-coulometry with reduction potential corresponding to the limiting current of the most negative cathodic wave the catholyte turns orange and later purple; toward the end of the electrolysis it becomes colourless and the total electron consumption gives $n = 9\cdot5$. This colourless solutions only exhibits two anodic waves whose $E_{1/2}$ is $-0\cdot33$ V (anodic wave of NO_2^-) and $-0\cdot68$ V. This later value corresponds to the anodic oxidation of dihydroacridine. In the catholyte only the presence of acridine (*X*) and dihydroacridine (*IX*) has been confirmed. In coulometric measurements of *II* in CH_3CN with 0·05M-$N(n\text{-}C_4H_9)_4PF_6$ and with acetic acid (2·5% by vol.) the electrolyte is colourless at the end of the electrolysis and shows an anodic wave with $E_{1/2} = -0\cdot40$ V (the wave of NO_2^-). The consumption is equivalent to $n = 7\cdot7$. In all coulometric measurements in acetonitrile (with 0·05 or 0·1M-$N(n\text{-}C_4H_9)_4PF_6$) the values obtained for a blank were subtracted.

Preparative Electrolysis

A $2\cdot5 \cdot 10^{-3}$ mol/l solution of *II* (272 mg) in acetonitrile with 0·05–0·1M-$N(n\text{-}C_4H_9)_4PF_6$ was reduced at a stirred mercury cathode. The anolyte contained 0·8 ml conc. H_2SO_4 in 50 ml ethanol. At the beginning the solution gives three cathodic waves. During electrolysis it gradually turns yellow and finally acquires an orange colouration. On passing a charge of 520 C through the solution (theoretical consumption is 582 C for $n = 6$) two new anodic waves form on the polarogram (at $-0\cdot55$ V and $-0\cdot9$ V, respectively). The solution is diluted with water and extracted with ether. The solvent is removed from the extract and the latter is once more extracted with ether. TLC analysis of the yellow oily residue pointed to the presence of acridine and acridone. For precise identification the mixture was separated by column chromatography.

The preparative electrolysis of *II* in anhydrous acetonitrile with 0·1M-$N(n\text{-}C_4H_9)_4 \cdot PF_6$ and 0·5% (by vol.) acetic acid (a cathodic wave at $-2\cdot2$ V was found before electrolysis) led to the appearance of an anodic wave at $-0\cdot5$ V and a cathodic wave at approx. $-2\cdot0$ V of the product after the consumption of a charge equal to 990 C($n = 10\cdot2$). The samples taken at intervals during electrolysis and subjected to TLC analysis reveal increasing quantities of 2,2'-diaminobenzophenone. Acridone (*XVII*) is a minor product, no acridine (*X*) has been found.

Isolated Products and Their Polarographic Behaviour

2,2'-Diaminobenzophenone (*XI*) ($C_{13}H_{12}N_2O$, m.w. 212·09). A yellow crystalline compound (m.p. 130·5–131·5 °C) has been isolated by fractional crystallization from n-hexane of the reaction mixture after electrolysis containing 0·1M-$N(n-C_4H_9)_4$ . . PF_6 and about 10% (by vol.) ethanol (saturated with NH_3). After recrystallization from the same solvent the m.p. increased to 133–134°C (the literature[3] states that *XI* has a m.p. equal to 134–135°C). A polarographic investigation of the isolated compound in CH_3CN with 0·1M-$N(n-C_4H_9)_4PF_6$ shows a single cathodic wave at −2·26 V. An addition of conc. acetic acid, however, makes this wave disappear. In polarography of *XI* in 0·1M-HCl with 50% ethanol a cathodic wave appears with $E_{1/2} = -1{\cdot}22$ V, in solutions with pH 2·9 50% ethanol $E_{1/2} = -1{\cdot}26$ V and in 0·2M-NaOH with 50% ethanol $E_{1/2} = -2{\cdot}0$ V. In a similar manner the cathodic waves observed in water–ethanolic solution of buffers, acids or hydroxides disappear on adding concentrated acetic acid. In microcoulometric analysis of *XI* in CH_3CN (with 0·1M-$N(n-C_4H_9)_4PF_6$) the yellow catholyte fully discolours and an anodic wave at $E_{1/2} = -0{\cdot}83$ V appears ($E_{1/2}$ of dihydroacridine is −0·74 V). The seal of the coulometric cell (the seal is filled with the Nessler reagent with a small amount of MgO) turns yellow: a positive test for the presence of ammonia. The mass spectra of the substance show M^+ 212 *m/e*, and further fragments 211 *m/e*, 196 *m/e*, 120 *m/e*, 93 *m/e*. The IR spectra were recorded with a KBr pellet and exhibit the following vibrational bands: 3 440cm^{-1} (m), 3 340 cm^{-1} (m), 2 930 cm^{-1} (w), 1 610 cm^{-1} (s), 1 480 cm^{-1} (m), 1 450 cm^{-1} (m), 1 300 cm^{-1} (s), 1 240 cm^{-1} (s). Both the polarographic behaviour and the above spectral data confirmed the ascription of the substance to the structure *XI*.

Acridone (XVII), m.p. 354°C. This model compound gives a cathodic wave at $E_{1/2} = -2{\cdot}30$ V in CH_3CN with 0·1M-$N(n-C_4H_9)_4PF_6$ (with a HMDE $E_p \doteq -2{\cdot}0$ V in ac-polarography $E_p = -2{\cdot}28$ V). In several cases a more positive cathodic wave was also observed with $E_{1/2} = -2{\cdot}10$ V. Yet, this substance exhibits a very low solubility which causes disturbances on the polarographic curves, in particular if it is formed at the dropping mercury electrode surface during electrolysis of *II*.

Acridine (X), m.p. 107–110°C, has been isolated by chromatography in a benzene–ether system on a poured silica gel column. Its identity has been proved by comparing it with a standard and by mass spectra. This spectra contains fragments 179 *m/e*, 151 *m/e* and 152 *m/e*. Its solution in CH_3CN with 0·05M-$N(n-C_4H_9)_4PF_6$ gives a cathodic wave with $E_{1/2} = -1{\cdot}84$ V (with HMDE, $E_p = -1{\cdot}74$ V). In microcoulometry an anodic wave is formed with $E_{1/2} = -0{\cdot}78$ V. On oxidizing by air the dihydroacridine formed by the electrolytical reduction a cathodic wave at −2·40 V develops; this wave corresponds to the reduction of acridone (*XVII*). With acridine the Kalousek commutator yielded an anodic wave with $E_{1/2} = -0{\cdot}74$ V on the commutated curve ($E_{aux} = -2{\cdot}0$ V) in the above media. For water–ethanolic solutions the irreversible polarographic behaviour of acridine had been already described by Kaye and coworkers[10] and our results fully accord with these reported by this research group.

Dibenzo[b, e]-(1,2)-*diazepin*-11-*one* (XII) was prepared as a model compound. In water–ethanolic solutions (50% ethanol by vol.) it gives three cathodic waves of approx. the same height over a broad range of pH-values (Table III). cp-Coulometric measurements at pH 2·9 with reduction potential adjusted to the region of the limiting current of the middle (second) cathodic wave give n equal to 3·8; $E_{1/2}$ of the anodic wave is −0·31 V. With the reduction potential in the region of the most negative cathodic wave *n* equal to 6·1 is obtained, the catholyte discolours and no wave can be observed. Commutated curves (Kalousek commutator) with the generation potential in the region of the limiting current of the most positive cathodic wave always exhibit an anodic wave with $E_{1/2}$ almost identcial with that of the most positive cathodic wave; this behaviour is characteristical for the whole pH range studied here. In the acid region and with the generating potential in the region of the most negative cathodic wave the anodic wave on the commutated curve becomes indistinct. Our polarographic results are in accord with those reported by Johns and Markham[5]. In addition to their findings, however, we have detected a third, most negative cathodic wave which doubtlessly reveals the electrolytical reduction of the carbonyl group. We propose Scheme 2 for the mechanism of the electrolytical reduction: in the first, most positive, reversible wave the dihydro derivative is formed. In the subsequent two more negative cathodic waves an irreversible reduction of the carbonyl group takes place which, however, does not lead to the formation of dihydrodibenzodiazepine (*XV*).

CONCLUSIONS

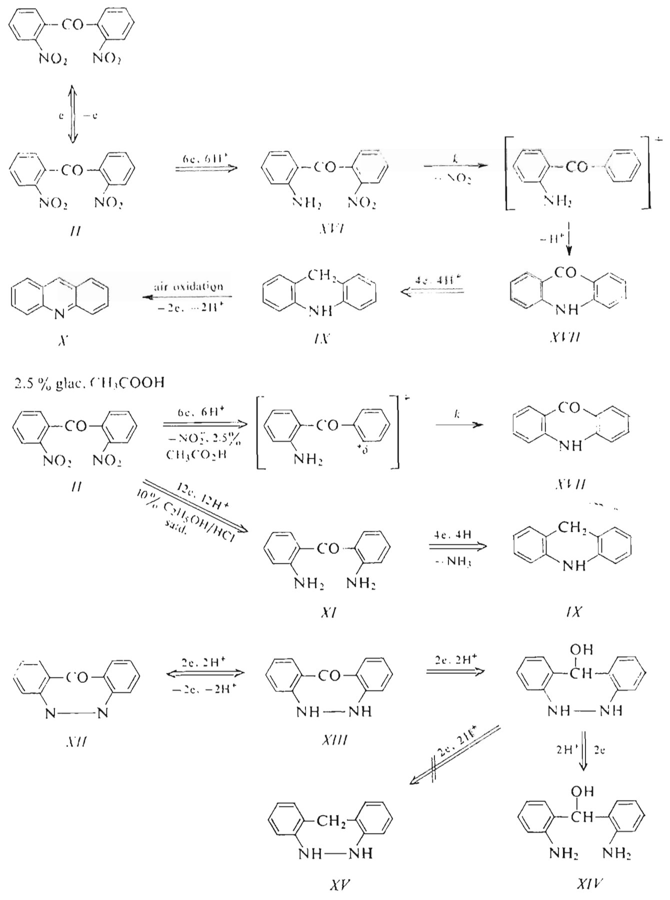
The last two dinitro compounds in the studied series *I* and *II* reduce in a different way on mercury electrodes. Owing to the CH_2 link between the two nuclei the conjugation is interrupted. Its electrolysis proceeds with an uptake of 8 electrons with the formation of a bishydroxylamino derivative. In spite of the fact that during electro-

TABLE III

Dependence of half-wave potentials of $5 . 10^{-4}$M dibenzo[*b*,*e*]-(1,2)-diazepin-4-one on pH in buffered solutions (50% by vol. ethanol)

pH	$-E_{1/2}$	V, *vs*	S.M.E.
0·9	0·24	0·93	1·20
2·9	0·31	1·05	1·31
9·0	0·64	1·55	1·93
12·4	0·93	1·74	2·06

Mechanism of Electrochemical Behaviour of Dinitro Compound



SCHEME 2

lysis this intermediate is not subject to intramolecular disproportionation leading to the formation of dibenzodiazepine, it cannot be isolated. The increase in its concentration during isolation cause intermolecular disproportionation in which *IV* results. As regards this intermolecular disproportionation mechanism yielding a cyclic azoxy compound, 2,2'-dinitrodiphenylmethane is an exception in our series.

The second substance, *II*, because of difficulties arising from its poor solubility, was studied in anhydrous acetonitrile. This is why its behaviour cannot be simply compared to that of *I* or of the other analogues. As follows from its structure the CO group ensures a perfect conjugation through the whole system. Moreover, the orientation of the nitro groups in the compound makes possible a single-step 6-electron electrolytical reduction to 2 nitro-2'-aminobenzophenone. In acetonitrile, this intermediate splits off the other, unchanged nitro group as a nitrite anion. This chemical elimination is followed by a follow-up cyclization reaction giving rise to acridone. At a more negative potential this product reduces in a 4-electron wave and 9,10-dihydroacridine results. The electrolytical reduction of a ketone to a CH_2 group only takes places owing to the acridone intermediate. A seven-membered heterocyclic dibenzodiazepinone is not formed.

The comparison of the electrochemical behaviour of all 2,2'-dinitro derivatives in the 2,2'-dinitrodiphenyl – X series has indicated that the ease of the electrolytical reduction decreases – according to X – in the following sequence: CO > O > S and CH_2 > NH. The position of the NH analogue as that the reduction of which is the most difficult is not quite correct since $E_{1/2}$ of the first reduction step was considered which is – not very distinctly – split into two waves. It was not possible to determine $E_{1/2}$ of the most positive cathodic wave. Structural criteria in accordance with actual reduction mechanisms resulted in separating the compounds into two groups: The analogues with O, CH_2 and S as the connecting link yield bis-hydroxylamine after an 8-electron transfer. The stability of this key intermediate decides about the composition of final products. In analogues with the S-or O-link the above-mentioned bis-hydroxylamines undergo an intramolecular disproportionation resulting in the formation of dibenzodiazepine structures whereas the intermediate of the CH_2-analogue disproportionates in an intermolecular reaction not sooner than during isolation and forms dibenzodiazepin N-oxide structures.

The analogoues with CO- and NH-links constitute an other group as regards the reaction mechanism. Their structure is a good prerequisite of a one-step 6-electron reduction of one of the nitro groups[6], *i.e.* of a partial electrolytical reduction. The 2,2'-nitroamino derivative was isolated in case of the NH-analogue. The electrolytical reduction of the other nitro group occurs in a more negative 4-electron wave. Instead of an intramolecular cyclization with the formation of dihydrodibenzotriazepine, the intermediate thus formed eliminates a NHOH-group together with the electron pair and is transformed to dihydrophenazine. The hydroxylamine set free in this way undergoes a chemical follow-up reaction and gives rise to nitrogen, simultaneously, however it oxidizes phenazine to phenazine N-oxide. The described nitrogen elimination occurs over a broad range of pH-values. The electrolytical reduction of the CO--analogue – even if performed in non-aqueous media – distantly resembles the mechanism of the NH-analogues *viz.* by the splitting off of one NO_2-group as NO_2^- or by the formation of acridine structures. The isolated 2-amino-2'-nitrodiphenylamine undergoes an anomalous electrolytical reduction as compared *e.g.* to 2-amino-2'--nitrodiphenyl since after a 4-electron reduction to the hydroxylamine intermediate an hydroxylamine elimination proceeds as described above.

In dibenzo(X) diazepine products (X = O, S, CO) the ease of their reduction decreases in the sequence S < O < CO. Nevertheless, it holds true for all 2,2'-dinitro compounds of our series that they are reduced at more negative potentials than the corresponding 7-membered dibenzo(X) diazepines prepared from them. The tendency of the reduced forms of these compounds to disproportionate has not been studied but it can be of great importance as regards the yield of dibenzo(X)diazepine products. All dibenzo(X)diazepines studied in this and preceding communications (*i.e.* X = O, S, CO) exhibit an electrochemically reversible behaviour this being in accordance with the conception that they can be looked upon as substituted azobenzenes.

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