POLAROGRAPHY AND CONTROLLED POTENTIAL ELECTROLYSIS OF SOME GEMINAL OR α-SUBSTITUTED α-ETHYLENIC NITRO DERIVATIVES
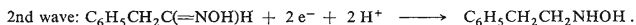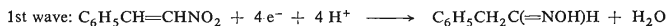
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$C_6H_5CH{=}C(Br)NO_2$ is reduced in a water–dioxane medium into $C_6H_5{-}CH_2{-}C{\equiv}N$ and Br^- according to a six electrons process; in a water–methanol medium $C_6H_5{-}CH(OCH_3)C{\equiv}N$ is isolated in addition to the preceding compounds, this allows to propose a reduction mechanism. At every pH $CH_3C(NO_2){=}C(NO_2)CH_3$ is reduced according to a reversible bielectronic primary process; a reduction mechanism is proposed which allows to explain the formation of the electrolysis products: diacetyl, diacetyl monoxime, dimethylglyoxime and dimethylfuroxan. The polarographic behaviour of some other dinitro derivatives is also studied.

The electrochemical reduction on a mercury pool, in an hydroorganic medium of α-ethylenic nitro derivatives has been dealt with in several studies. The β-nitrostyrene, a typical compound in these series, shows between pH 1 and 11 a four electrons wave the $E_{1/2}$ of which is a linear function of pH unto pH 7 ($E_{1/2} = -0.023 - 0.063$ pH in a 90 : 10 water–ethanol medium) and then becomes pH independent at higher pH (ref.[1]). Between pH 1 and 3 a second wave is observed which corresponds to a two electrons reduction. Electrolysis have been carried out on the first and on the second plateau by Masui and Sayo[2,3]; they isolated phenylacetaldoxime and β-phenethylhydroxylamine and propose the following reduction mechanism:

1st wave: $C_6H_5CH{=}CHNO_2 + 4e^- + 4H^+ \longrightarrow C_6H_5CH_2C({=}NOH)H + H_2O$

2nd wave: $C_6H_5CH_2C({=}NOH)H + 2e^- + 2H^+ \longrightarrow C_6H_5CH_2CH_2NHOH$.

The same behaviour is evidenced by other nitro olefins[4,5]. In a general way the $E_{1/2}$ of the first wave are more positive by several hundred millivolts than that of the first wave of the corresponding, saturated nitro derivatives.

The electrochemical reduction of gem- or α-substituted α-ethylenic nitro derivatives is undertaken in order to bring forward the influence of the substituent on the reduction mechanism.

THE STUDY OF β-BROMO-β-NITROSTYRENE $C_6H_5CH=C(Br)NO_2$ AT pH 1−7

Polarography: A single 6 electrons wave (by comparison with the 4 electrons wave of β-nitrostyrene) is observed, its $E_{1/2}$ depends in a essentially linear manner on the pH; $C_6H_5CH=C(Cl)NO_2$ shows similar polarograms. As it can be seen from Table I the half-wave potentials of $C_6H_5CH=C(Br)NO_2$ and $C_6H_5CH==C(Cl)NO_2$ are very close: thus the substitution of Br by Cl brings practically no changes on the $E_{1/2}$ values. Controlled potential electrolysis in dilute solutions ($c = 2$ or $4 . 10^{-3}$M) carried out in water–dioxane or water–methanol at different potentials (on the plateau of the first wave) show that between 5·5 and 6 electrons are consumed per molecule of $C_6H_5CH=C(Br)NO_2$. The electrolysed solution does not give any polarogram; its UV spectrum shows at $\lambda > 225$ nm the characteristic bands of an unconjugated phenyl group.

Preparative electrolysis: Water–methanol or water–dioxane mediums are used, the concentrations are between 0·05M and 0·1M, the pH is close to 1 (H_2SO_4), the cathode potential is maintained at $-0·4$ V. The number of electrons per molecule is between 5 and 6 and lower in water–methanol than in water–dioxane. At the end of the electrolysis, water is added to the solutions which are then extracted with ether. The oily product accounts for about 50 to 60% of the weight of the starting compound. The different derivatives obtained in this oily product are separated by preparative gas liquid chromatography. In the aqueous layer a potentiometric titration evidences about 90% of Br^- (by reference to $C_6H_5CH=C(Br)NO_2$). In a water–dioxane mixture two main compounds are isolated: $C_6H_5CH_2C\equiv N$ (80%) and C_6H_5CHO (10%), in water–methanol three main compounds are isolated: $C_6H_5CH_2C\equiv N$, $C_6H_5CH(OCH_3)C\equiv N$ and C_6H_5CHO.* The percentage of this last compound is always about 10% while that of the two others lies around 80%. The amount of $C_6H_5CH(OCH_3)C\equiv N$ increases with the concentration of $C_6H_5CH==C(Br)NO_2$: thus its yield is about 20% for $c = 0·05$M and reaches 35−40% for $c = 0·01$M.

Reduction Mechanism

As the benzaldehyde is probably obtained through the partial hydrolysis of $C_6H_5CH=C(Br)NO_2$, the phenylacetonitrile appears as the principal reduction product

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*   Some reductions of $C_6H_5CH=C(Br)NO_2$ have been carried out by chemical ways with zinc and acetic or sulfuric acid, either in an heterogeneous medium (water–ether) or in a water–methanol mixture. In every case the main isolated product is phenylacetonitrile.

TABLE I
Half-Wave Potentials ($E_{1/2}$, vs. SCE) of $C_6H_5CH=C(X)NO_2$ in 40% Methanol

pH	1	2	3	4	5	6	7
X = H	−0·08	−0·18	−0·24$_5$	−0·31$_5$	−0·38$_5$	−0·42$_5$	−0·49$_5$
X = Br	−0·06	−0·15	−0·20	−0·25	−0·30	−0·35	−0·40
X = Cl	−0·04	−0·12	−0·18	−0·25	−0·31	−0·36	−0·42

in water–dioxane. The polarographic data, as well as the results of the dilute solution electrolysis and of the electrolysis in water–dioxane ($c = 0·1M$) agree with the following overall reduction mechanism:

$$C_6H_5CH=C(Br)NO_2 + 6\,e^- + 5\,H^+ \longrightarrow C_6H_5CH_2C\equiv N + Br^- + 2\,H_2O\,.$$

In water–methanol the formation of $C_6H_5CH(OCH_3)C\equiv N$ may be explained by an attack of methanol on $C_6H_5CH\overset{(+)}{-}C\equiv N$ this last compound being obtained after the fixation of 4 electrons and 4 protons.

In order to explain this overall reaction a comparison can be made either with the reduction mechanism of aliphatic gem-bromonitro derivatives, or with that of β-nitrostyrene.

a) The electrochemical reduction of saturated gem-bromonitro derivatives proceeds[6] according to equation:

$$R^1R^2C(Br)NO_2 + 2\,e^- \longrightarrow R^1R^2C=NO_2^{(-)} + Br^-\,.$$

In all the studied cases a two electrons wave is observed the $E_{1/2}$ of which is pH independent. In our case the $E_{1/2}$ depends on the pH; besides $C_6H_5CH=C=NO_2^{(-)}$ (or $C_6H_5CH=C=NO_2H$) would be obtained, this compound would probably have a very low stability and would be less reducible than the starting compound. This compound could undergo rearrangement into β-nitrostyrene, but as this last compound has a more negative half-wave potential than $C_6H_5CH=C(Br)NO_2$ a two electrons wave should be observed followed by the two waves of β-nitrostyrene. This is different from what is observed. Moreover controlled potential electrolysis would lead to $C_6H_5CH_2C(=NOH)H$.

b) The following equation must also be excluded on the basis of some reasons explained in a):

$$C_6H_5CH=C(Br)NO_2 + 2\,e^- + H^+ \longrightarrow C_6H_5CH=CHNO_2 + Br^-\,.$$
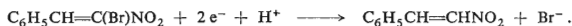
c) As the half-wave potentials depend on the pH and are very close from that of β-nitrostyrene the nitro group can be supposed to be first reduced. If an equation analogous to that of the β-nitrostyrene reduction is taken into account:

$$C_6H_5CH{=}C(Br)NO_2 + 4\,e^- + 4\,H^+ \longrightarrow C_6H_5CH_2C({=}NOH)Br + H_2O$$
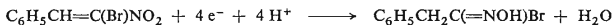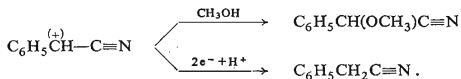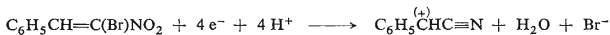
an oxime of acid bromide would be obtained. These compounds are likely to give nitrile oxides which are chemically reducible into nitrile[7]:

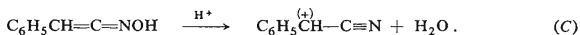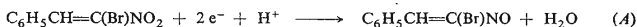$$RC({=}NOH)Br \longrightarrow RC{\equiv}N{\rightarrow}O + Br^- + H^+$$
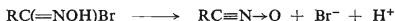
Several facts stand against this mechanism. First of all the nitrile oxides are reduced[8,9] at the dropping mercury electrode according to equation:

$$RC{\equiv}N{\rightarrow}O + 2\,e^- + 2\,H^+ \longrightarrow RC({=}NOH)H\,.$$
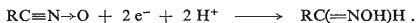
It has been checked that $C_6H_5CH_2C{\equiv}N{\rightarrow}O$ gives a two electrons wave followed by that of $C_6H_5CH_2C({=}NOH)H$; this last wave is missing on the polarogram of $C_6H_5CH{=}C(Br)NO_2$. Besides $C_6H_5CH{=}C(Cl)NO_2$ gives a six electrons wave (by reference to the 4 electrons wave of $C_6H_5CH{=}CHNO_2$) in hydrochloric medium while under the same conditions $C_6H_5CH_2C({=}NOH)Cl$ does not give any wave, as it has been checked. At last it would be difficult to explain the formation of $C_6H_5.$ $.CH(OCH_3)C{\equiv}N$; methanol can actually react with nitrile oxides under certain conditions but in this case compounds of $RC(OCH_3){=}NOH$ type are obtained[7]. The simultaneous formation of $C_6H_5CH_2C{\equiv}N$ and $C_6H_5CH(OCH_3)C{\equiv}N$ in water–methanol is easily explained if the formation of the ion $C_6H_5\overset{+}{C}HC{\equiv}N$ is admitted. Thereof a two steps mechanism is proposed to explain the reduction into benzyl cyanide:

$$C_6H_5CH{=}C(Br)NO_2 + 4\,e^- + 4\,H^+ \longrightarrow C_6H_5\overset{(+)}{C}HC{\equiv}N + H_2O + Br^-$$

$$C_6H_5\overset{(+)}{C}H{-}C{\equiv}N \quad \Big\langle \quad \begin{array}{l} \xrightarrow{\;CH_3OH\;} \quad C_6H_5CH(OCH_3)C{\equiv}N \\[2mm] \xrightarrow{\;2e^-\,+H^+\;} \quad C_6H_5CH_2C{\equiv}N\,. \end{array}$$

The first 4 electrons step is rather uneasy to explain. The significant variation of $E_{1/2}$ with pH as well as the close values of the half-wave potentials of $C_6H_5CH{=}C(Br).$ $.NO_2$, $C_6H_5CH{=}C(Cl)NO_2$ and $C_6H_5CH{=}CHNO_2$ allow to think, as said earlier, that the NO_2 group undergoes the first electronic attack. The following succession can be taken into account:

$$C_6H_5CH=C(Br)NO_2 + 2\,e^- + H^+ \longrightarrow C_6H_5CH=C(Br)NO + H_2O \qquad (A)$$

$$C_6H_5CH=C(Br)NO + 2\,e^- + H^+ \longrightarrow C_6H_5CH=C=NOH + Br^- \qquad (B)$$

$$C_6H_5CH=C=NOH \xrightarrow{\ H^+\ } C_6H_5\overset{(+)}{C}H-C\equiv N + H_2O . \qquad (C)$$

The step (A) is likely to occur as the saturated nitro derivatives are first reduced into nitroso derivatives; the step (B) is exactly similar to the reduction Scheme of the saturated gem-bromonitroso derivatives[6].

THE STUDY OF cis-2,3-DINITRO-2BUTENE

Polarography: Between pH 1 and 12, *cis* 2,3 dinitro-2-butene presents a first two electrons wave (by reference to 2 nitropropane 4 electrons), its $E_{1/2}$ depends on the pH in acidic medium (Fig. 1). At pH lower than 6 the polarogram presents a second wave the half-wave potential of which is highly pH dependent $\left(-0.8\text{ V at pH 1};\right.$ -1.1 V at pH 2$\left.\right)$. Unto pH 2 the wave is well defined and its height is about five times that of the first wave; the height of this wave decreases rapidly and disappears over pH 6.

Controlled potential electrolysis in dilute solution $\left(c = 4\,.\,10^{-3}\text{M}\right)$: At pH 2·6 and at 20°C (25% methanol; $E = -0.2$ V) 1·9 electrons are consumed per molecule. The polarogram and the ultra violet spectrum of the electrolysed solution lead to think that it contains 2-nitro-2-butene and diacetyl monoxime. The concentrations are respectively evaluated to about $1.5\,.\,10^{-3}$M and $1\,.\,10^{-3}$M. At pH 6 and at 20°C $\left(E = -0.4\text{ V}\right)$ 1·75 electrons are consumed per molecule. The polarogram and the ultra-violet spectrum point to the presence of 2-nitro-2-butene at a concentration of about $2.2\,.\,10^{-3}$M. At pH 7 and at 3°C $(E = -0.4$ V) 1·75 electrons are consumed per molecule. The polarogram of the electrolysed solution A shows an anodic wave the height of which is about $45-50\%$ of that of the wave of *cis*-2,3-dinitro-2-butene before the electrolysis. If the temperature of the solution A is raised to 20°C the anodic
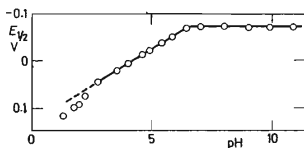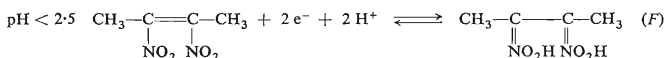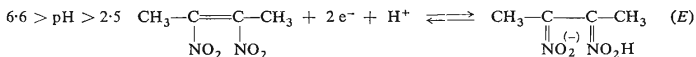

Fig. 1

Half-Wave Potentials of *cis*-CH$_3$C(NO$_2$)=C.(NO$_2$)CH$_3$

wave disappears slowly and simultaneously a cathodic wave appears which is attributed to 2-nitro-2-butene; the concentration of this compound reaches about $2.2 \cdot 10^{-3}$M. An electrochemical oxidation of solution A at 3°C $(E = +0.15 \text{ V})$ gives *cis*-2,3-dinitro-2-butene (the polarograms of the oxidised solution at different pH are identical with those of the authentic sample); the height of the cathodic wave of *cis*-2,3-dinitro-2-butene is close to that of the anodic wave of solution A. The number of coulombs consumed during the oxidation is in good agreement with a bielectronic process.

Controlled potential electrolysis at 0·1M *concentration*: At pH $1-1.5$ and at 20°C (50% acetonitrile; $E = -0.2$ V) about 2·9 electrons are consumed per molecule. The solution becomes blue at the very beginning of the electrolysis at the end it is colourless. Once the electrolysis is finished, the solution is extracted with ether to give a partially cristalline mixture containing (gas–liquid chromatography) diacetyl, diacetyl monoxime and dimethylfuroxan. The crystals were identified as dimethylglyoxime. Under the same conditions but using methanol instead of acetonitrile about 2·7 electrons are consumed per molecule; the blue colour also appears during the electrolysis. By working up the mixture as before diacetyl, diacetyl monoxime and dimethylfuroxan are isolated. At pH $4-4.5$ in water–methanol or water–acetonitrile the number of electrons per molecule lies between 1·7 and 2·1. The solution does not become blue during the electrolysis. The same compounds are isolated as at pH $1-1.5$.

Reduction Mechanism

Although neither the α-dinitronates nor the corresponding nitronic acids have been described and though it was not possible to isolate these compounds the following scheme seems to accounts correctly for the experimental results:

$$\text{pH} > 6.6 \quad \begin{matrix} CH_3-C=C-CH_3 \\ | \quad\;\; | \\ NO_2 \;\; NO_2 \end{matrix} + 2\,e^- \;\rightleftharpoons\; \begin{matrix} CH_3-C\!-\!-\!-\!C-CH_3 \\ \| \,_{(-)} \;\; \| \,_{(-)} \\ NO_2 \quad NO_2 \end{matrix} \quad (D)$$

$$6.6 > \text{pH} > 2.5 \quad \begin{matrix} CH_3-C=C-CH_3 \\ | \quad\;\; | \\ NO_2 \;\; NO_2 \end{matrix} + 2\,e^- + H^+ \;\rightleftharpoons\; \begin{matrix} CH_3-C\!-\!-\!-\!C-CH_3 \\ \| \,_{(-)} \;\; \| \\ NO_2 \quad NO_2H \end{matrix} \quad (E)$$

$$\text{pH} < 2.5 \quad \begin{matrix} CH_3-C=C-CH_3 \\ | \quad\;\; | \\ NO_2 \;\; NO_2 \end{matrix} + 2\,e^- + 2\,H^+ \;\rightleftharpoons\; \begin{matrix} CH_3-C\!-\!-\!-\!C-CH_3 \\ \| \quad\;\; \| \\ NO_2H \;\; NO_2H \end{matrix} \quad (F)$$
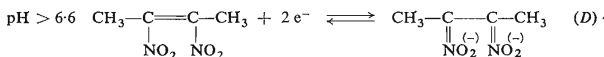
At pH higher than 6·6 a single two electrons wave is observed on polarograms, its half-wave potential is pH independent. The absence of a second wave agrees with the formation of a dinitronate ion as it is known that the nitronate ions $>C=NO_2^{(-)}$, at the contrary of nitro groups, are not reducible at the dropping mercury electrode.

The nitronic acids $R^1(R^2)C=NO_2H$ give, between pH 0 and 2, a two electrons polarographic wave corresponding to the reduction into an oxime[6], the height of the wave decreases rapidly when the pH increases. The equation (F) thus gives a possible explanation of the second observed wave. As a matter of fact, at pH $1-1.5$, this wave is about 1.5 times higher than that of dimethylglyoxime (polarographed under the same conditions). This last compound is known to give an eight electrons wave (corresponding to the reduction into 2,3-diaminobutane), its $E_{1/2}$ is close from that of the second wave of *cis*-2,3-dinitro-2-butene. Thus, the second wave, around pH 1, could be explained by the following Scheme:
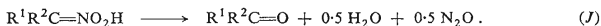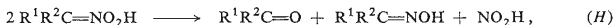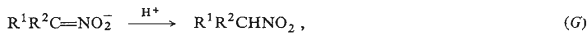
$$CH_3C(=NO_2H)—C(=NO_2H)CH_3 + 12\,e^- + 12\,H^+ \longrightarrow$$

$$\longrightarrow CH_3C(H)(NH_2)—C(H)(NH_2)CH_3 + 4\,H_2O$$
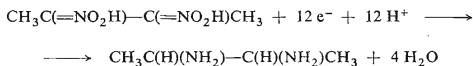
The electrochemical reversibility implied by schemes (D), (E), and (F) is proved by cyclic voltammetry with a triangular voltage sweep. At different pH and at $v = 0.5\ \text{V s}^{-1}$ the presence of an anodic peak of the same height as the cathodic peak of *cis*-2,3-dinitro-2-butene is observed. The difference between the potentials of the two peaks agrees with the theoretical value of bielectronic reversible system.

The number of electrons per molecule involved in the controlled potential electrolysis is, as it has been seen, about 2, except in the case of electrolysis carried out at pH $1-1.5$ with 0.1M concentration.
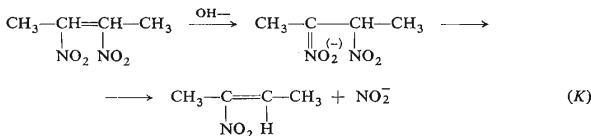
It has been seen that the controlled potential electrolysis at low concentration give among other products 2-nitro-2-butene while at 0.1M concentration diacetyl, diacetyl monoxime and dimethylfuroxan are obtained. On the basis of the behaviour of nitronic acids in aqueous mediums[10], the obtention of all these compounds can be rationalised.

As a matter of fact, the nitronic acids deriving from secondary nitro compounds are known to undergo three main reactions, each of them prevailing in a certain pH range. Thus, when the pH decreases:

$$R^1R^2C=NO_2^- \xrightarrow{\ H^+\ } R^1R^2CHNO_2\,, \tag{G}$$

$$2\,R^1R^2C=NO_2H \longrightarrow R^1R^2C=O + R^1R^2C=NOH + NO_2H\,, \tag{H}$$

$$R^1R^2C=NO_2H \longrightarrow R^1R^2C=O + 0.5\,H_2O + 0.5\,N_2O\,. \tag{J}$$

Each of the $>C=NO_2H$ groups of the dinitronic acid can undergo the reactions (H) and (J), thus explaining satisfactorily the presence of diacetyl, of its oximes and of dimethylfuroxan, as this last compound can be prepared[11] by cyclisation of $CH_3C(=NO_2H)C(=NOH)CH_3$.

Studies on the transformation of nitronic acids $R^1R^2C=NO_2H$ have shown[10] that NO_2H formed in the reaction (H) reacts with $R^1R^2C=NO_2H$, in acidic medium, to give a blue pseudonitrol $R^1R^2C(NO)NO_2$; this last compound is easily electro-reducible into an oxime[6]. On the other hand the reaction (J), Nef reaction, involves a blue nitroso compounds as an intermediate. All these considerations give a reasonable justification of the blue colour observed during the electrolysis with 0·1M concentration at pH 1—1·5 and of the number of electrons involved (higher than 2). The formation of 2-nitro-2-butene can also be explained: a recent study[12] allows to write the following reaction mechanism (Eq. (K)):

$$
\begin{array}{c}
CH_3-CH=CH-CH_3 \xrightarrow{\ OH- \ } CH_3-C-\!-CH-CH_3 \longrightarrow \\
\quad | \quad\quad\ | \qquad\qquad\qquad\qquad \| \ \ (-)\ | \\
\ \ NO_2\ \ NO_2 \qquad\qquad\qquad\quad NO_2\ \ NO_2
\end{array}
$$

$$
\longrightarrow\ CH_3-C=\!=C-CH_3\ +\ NO_2^- \qquad\qquad (K)
$$
$$
\qquad\qquad | \quad\ |
$$
$$
\qquad\qquad NO_2\ \ H
$$

The reaction (G) applied to one of the two $>\!C=NO_2^{(-)}$ functions of the dinitronate leads precisely to the $CH_3C(NO_2)(H)-C(=NO_2^{(-)})CH_3$ ion.

The chromatograms of the oil obtained from the electrolysis at 0·1M concentrations show that the 2-nitro-2-butene content is lower than 10% (if any) while it is about 50% in the case of the low concentration electrolysis. It seems likely that some of the reactions leading to diacetyl, to its oximes and to dimethylfuroxan be of an higher order than that of the reaction leading to 2-nitro-2-butene.

Some tentative isolations of a salt corresponding to the hypothetic dinitronate of reaction (D) were unsuccessful. As reaction (K) excludes its formation from 2,3-dinitrobutane, the precipitation of a baryum salt in a solution electrolysed at pH 7 $(c = 0·1M;\ t\ 3°C)$ has been first tried, then the reductions of cis-2,3-dinitro-2-butene by sodium in liquid ammonia, or potassium in benzene or sodium in methanol were also unsuccessful.

trans-$CH_3C(NO_2)=C(NO_2)CH_3$ presents polarograms and $E_{1/2}$ identical to those of cis isomer. The electrolysis at different concentrations gives the same results as for cis isomer. Thus the stereochemistry of the molecule does not influence its reduction mechanism. cis-$C_2H_5C(NO_2)=C(NO_2)C_2H_5$ shows the same polarograms as cis-2,3-dinitro-2-butene with slightly more negative half-wave potentials $(\Delta E_{1/2} = = -0·04\ V)$. cis and trans-$C_6H_5C(NO_2)=C(NO_2)C_6H_5$ present at pH higher than 7 a two electrons wave the $E_{1/2}$ of which is close from that of cis-2,3-dinitro-2-butene (pH > 7, $E_{1/2} = -0·02\ V$); between pH 1 and 7 a two electrons wave is evidenced, its $E_{1/2}$ is slighty less negative than that of cis-2,3-dinitro-2-butene $(\Delta E_{1/2} = = +0·05\ V)$. This wave is followed by two others, the third is remindful of the second wave of cis-2,3-dinitro-2-butene. The second wave is attributed to $C_6H_5C(NO_2)=$

$=C(H)C_6H_5$. An electrolysis on the first plateau $(c = 2 . 10^{-3}M)$ consumes about 1·8 electrons per molecule; the polarogram and the UV spectrum of the electrolysed solution show the presence of *cis*-α-nitro stilbene $(c = 1·2 . 10^{-3}M)$. The height of the second wave (equal to 4 electrons or smaller) depends on the pH, the concentration and the nature of the buffer, thus it is supposed to be a kinetic wave: this would agree with a reaction analogous to (Eq. (K)).

The polarograms and the electrolysis at different concentrations carried out with *cis*-$CH_3C(NO_2)$=$C(NO_2)CH_3$ allow to bring forward a very original mechanism completely different from that of the simple α-ethylenic nitro derivatives. The primary bielectronic reduction process is reversible in the studied pH range. The polarograms of other nitro derivatives allow to think that this mechanism is general for the $RC(NO_2)$=$C(NO_2)R$ derivatives.

EXPERIMENTAL

Methods

The polarograms were drawn with a Radiometer PO_4 polarograph; the half wave potentials were corrected for the ohmic drop and given by reference to the aqueous saturated calomel electrode. A Radiometer model 4 pH meter was used for pH measurements. The controlled potentials electrolysis were carried out in a classical device with separated concentrical compartments of cylindrical shape. The cathode was a mercury pool stirred with a magnetic stirrer, the anode was a platinum sheet. The voltage difference between the cathode and the reference electrode was maintained constant with the help of a Tacussel (ASA 100—1 or ASA 10·10) potentiostat. The number of coulombs was measured with a Tacussel IG 4 10 000 integrator. The cell was provided with a thermostatic device.

The NMR spectra were drawn with the help of a varian A-60 spectrometer tetramethylsilane being used as internal reference, δ are given in p.p.m. The IR spectra were recorded with a Perkin-Elmer spectrometer model 21, and the UV spectra with an Unicam SP 800.

The gas phase chromatography has been carried out with a Varian Aerograph model 90 P on silicon SE 30 columns.

β-Bromo-β-nitrostyrene

Preparation of compounds. C_6H_5CH=$CHNO_2$. From C_6H_5CHO and CH_3NO_2 according to[13], m.p. 58°C. C_6H_5CH=$C(Br)NO_2$. By bromation of C_6H_5CH=$CHNO_2$ followed by debromhydratation according to[14], m.p. 68°C. NMR (deuteriochloroform): C_6H_5 multiplet (two protons) centered at δ = 7·8 and multiplet (three protons), centered at δ = 7·45; C_6H_5CH δ = 8·60 (singulet). C_6H_5CH=$C(Cl)NO_2$. By chloration of C_6H_5CH=$CHNO_2$ followed by dechlorhydratation according to[15], m.p. 49°C. NMR (deuteriochloroform): C_6H_5 multiplet (2 protons) centered at δ = 7·85 and multiplet (3 protons) centered at δ = 7·50; C_6H_5CH (singulet) δ = 8·37. $C_6H_5CH_2C$(=NOH)Cl. By chloration of phenylacetaldoxime according to[16], m.p. 90°C; NMR (hexadeuteriodimethyl sulfoxide): C_6H_5 multiplet centered at δ = 7·27; CH_2 singulet at 3·80; NOH singulet at 11·37. $C_6H_5CH(OCH_3)C$≡N. From $C_6H_5CH(OCH_3)$. .COOH (Fluka) according to[17]. NMR (tetrachloromethane): C_6H_5 (singulet) δ = 7·60; CH (singulet) δ = 5·16; OCH_3 (singulet) δ = 3.50.

Polarography. The used buffers were: H_2SO_4 or HCl, H_3PO_4–NaH_2PO_4, CH_3COOH–CH_3.
.COONa, NaH_2PO_4–Na_2HPO_4; their overall concentration was in the 0·1 to 0·2M
range. For $C_6H_5CH{=}CHNO_2$, $C_6H_5CH{=}C(Br)NO_2$, $C_6H_5CH{=}C(Cl)NO_2$ the solutions
contained 40% of methanol and the depolariser concentration was about 10^{-3}M. The same condi-
tions were used for $C_6H_5CH_2C({=}NOH)Cl$ and $C_6H_5CH_2C{\equiv}N{\to}O$, this last compound being
obtained *in situ* according to[7]. The halogeno derivatives of β-nitrostyrene give rise to maxima
which can be suppressed with the help of Triton X-100. The temperature was 25°C.

Dilute solution electrolysis. The potential was set between the electrodes before adding the
compound to be reduced in order to prevent the attack of mercury. The solution in the cathodic
compartment (200 ml) contained about 50% of co-solvent (methanol or dioxane) and an overall
buffer concentration equal or higher than 0·1M; the $C_6H_5CH{=}C(Br)NO_2$ concentration was
2 to 4 . 10^{-3}M. During the electrolysis argon was kept bubbling through the solution. The anodic
compartment had the same composition, but with no depolariser. The temperature was 25°C.
For example: the cathodic compartment containing 200 ml of a solution 50% in methanol and
0·25N in H_2SO_4: the voltage was set to $-0·4$ V and argon bubbled through the solution. When
$i < 2$ mA, 8 . 10^{-4} mol (183 mg) of $C_6H_5CH{=}C(Br)NO_2$ were introduced. When i became
again lower than 2 mA the electrolysis was stopped. The number of coulombs corresponded
to about 5·8 F/mol. A similar number of F/mol was found by extrapolating the number of cou-
lombs measured between the times t_1 and t_2, the concentration at t_1 and t_2 being measured
by UV spectrophotometry or by polarography.

Preparative electrolysis. The procedure was close from that precedingly described, the only
change was the composition of the cathodic compartment. The temperature was 25°C.

1. The cathodic compartment contained 200 ml of water–dioxane solution (80% dioxane)
with H_2SO_4 in 0·3M concentration. The cathode potential was set to $-0·4$ V and argon was
bubbled through the solution. When i was lower than 2 mA, 0·01 mol (2·28 g) of $C_6H_5CH{=}$
${=}C(Br)NO_2$ were introduced. The electrolysis was stopped when i was lower than 5 mA. The
number of electrons per molecule was about 5·8. 200 ml of water were added and the solution
extracted five times with 100 ml of ether. The etheral extracts were dried with magnesium sul-
phate. A potentiometric titration was carried out on the aqueous layer with a silver electrode:
it contained about 0·9 . 10^{-2}M Br^-. Ether and dioxane were evaporated under vacuum to give
1·15 g of oil. The analytical gas liquid chromatography evidenced two peaks *a* (10%) and *b* (80%).
The preparative gas–liquid chromatography allowed to isolate each of corresponding compounds;
the IR and NMR spectra showed, by comparison with authentic samples, that *a* was C_6H_5CHO
and *b* $C_6H_5CH_2C{\equiv}N$.

2. Dioxane was replaced by methanol and the same procedure as for *1.* was used. The number
of electrons per molecule was close to 5·4. 1·2 g of oil were obtained after extraction with ether
and evaporation of ether and methanol. The aqueous layer contained 0·9 . 10^{-2}M Br^-. The
chromatogram of the oil showed three peaks *a* (10%), *b* (65%) and *c* (20%). After separation
by preparative gas–liquid chromatography the IR and NMR spectra compared with those
of authentic samples showed that *a* C_6H_5CHO, *b* $C_6H_5CH_2CN$ and *c* $C_6H_5CH(OCH_3)CN$.

3. With the same procedure as for *2.* but with 0·02 mol of $C_6H_5CH{=}C(Br)NO_2$ the number
of electrons per molecule was close to 5·1. The aqueous layer contained about 1·7 . 10^{-2}M Br^-.
The oil obtained (2·5 g) by ether extraction and evaporation of ether and methanol contained
three compounds *a* (10%), *b* (45%) and *c* (35%) (percentage obtained by gas–liquid chromato-
graphy).

$RC(NO_2)=C(NO_2)R$ Derivatives

Preparation of the compounds. $CH_3C(NO_2)=C(NO_2)CH_3$. The *cis* derivative was obtained from $CH_3CH(Cl)(NO_2)$ according to[18]. NMR (tetrachloromethane): singulet at $\delta = 2\cdot33$. The *trans* derivative was obtained by reaction of N_2O_4 on 2-butyne[19]. *cis*-C_2H_5—$C(NO_2)=$ $=C(NO_2)C_2H_5$ was prepared from $C_2H_5CH(Cl)(NO_2)$ according to[18]. NMR (tetrachloromethane): CH_3 triplet centered at $\delta = 1\cdot23$, CH_2 quadruplet centered at $\delta = 2\cdot70$. *cis* and *trans* $C_6H_5C(NO_2)=C(NO_2)C_6H_5$ were synthetised by reaction of N_2O_4 with tolane[20]. NMR (hexadeuteriodimethyl sulfoxide): C_6H_5 multiplet centered at $\delta = 7\cdot4$ for the *cis* derivative and at $\delta = $ $= 7\cdot6$ for the *trans* derivative. $CH_3COCOCH_3$ was obtained from Schuchardt and redistilled. Diacetyl monoxime and dimethylglyoxime were obtained from Prolabo. Dimethylfuroxan was prepared by reaction of N_2O_4 with dimethylglyoxime in ether[21]. NMR (hexadeuteriodimethyl sulfoxide) CH_3 singulets at $\delta = 2\cdot11$ and $\delta = 2\cdot33$. 2-nitro-2-butene was prepared according to[22].

Polarography. The used buffers were H_2SO_4, H_3PO_4–NaH_2PO_4, CH_3COOH–CH_3COONa, NaH_2PO_4–Na_2HPO_4, $NaHCO_3$–Na_2CO_3, Na_2HPO_4–Na_3PO_4. Their overall concentration was in the $0\cdot1M$–$0\cdot2M$ range. The temperature was $20°C$. For the *cis* and *trans* 2,3-dinitro-2-butene and for *cis*-3,4-dinitro-3-hexene the depolariser concentration was $10^{-3}M$ or $2 . 10^{-3}M$; the solutions contained 20% of methanol or acetonitrile. For *cis* and *trans* $C_6H_5C(NO_2)=C(NO_2)$. .C_6H_5 the depolariser concentration was $2 . 10^{-4}M$ and solutions contained 40% of acetonitrile. The cyclic voltametry of *cis*-2,3-dinitro-2-butene was carried out with $6 . 10^{-5}M$ solutions containing 2% of acetonitrile. The sweep rate was $0\cdot5$ V s^{-1}.

Controlled potential electrolysis of $CH_3C(NO_2)=C(NO_2)CH_3$ in $0\cdot1M$ concentration *1*. The cathodic compartment contained 200 ml of solution (6 g H_2SO_4, 50% methanol). Argon was bubbled through the solution and the voltage was set to $-0\cdot2$ V. When $i < 2$ mA, $0\cdot02$ mol ($2\cdot92$ g) of depolariser were added. The solution very readily became blue but the colour faded with time. The electrolysis was stopped when i became lower than 5 mA, the number of electrons per molecule being about $2\cdot7$. The solution was extracted five times with 100 ml of ether, the etheral extracts were dried with magnesium sulphate and evaporated to give $2\cdot1$ g of an oil. Analytical and preparative gas–liquid chromatography allows to show the presence of diacetyl (20%), diacetyl monoxime (30%) and dimethylfuroxan (30%) among the ten compounds visible on the chromatogram.

2. The same procedure as for *1*. was used but methanol was replaced by acetonitrile. $2\cdot9$ electrons were consumed per molecule. By extraction with ether an oil ($3\cdot9$ g) was obtained which contained some crystals in suspension. The filtered crystals (200 mg) were shown to be dimethylglyoxime. The oil contained (gas–liquid chromatography) about 50% of remaining acetonitrile and about ten compounds among which diacetyl (8%), diacetyl monoxime (10%), dimethylfuroxan (20%).

3. The same procedure was used as for *1*. but with acetic acid (5 g) and sodium acetate ($1\cdot5$ g) as a buffer instead of sulphuric acid and the voltage was maintained at $-0\cdot3$ V. The solution did not become blue, but a yellow colour appeared at the end of the reduction. The number of electrons per molecule was about $1\cdot9$. The solution was extracted with ether, the etheral extracts were washed with a dilute sodium bicarbonate solution, dried with magnesium sulphate and evaporated to give an oil (2 g) which contained (gas–liquid chromatography) diacetyl (20%), diacetyl monoxime (40%) and dimethylfuroxan (20%).

4. The same procedure was used as for *3*. but with acetonitrile instead of methanol. The number of electrons per molecule was close to $1\cdot8$. The evaporation of the solution gave $4\cdot1$ g of an oil

containing some crystals. They were filtered (150 mg of dimethylglyoxime) and the oil was shown to contain (gas–liquid chromatography) diacetyl (10%), diacetyl monoxime (15%) and dimethyl-furoxan (15%) besides the remaining acetonitrile (50%).

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