Electrochemical reduction of quinoxalino[2,3-*b*]quinoxaline

JOSEPH ARMAND AND LINE BOULARES
Laboratoire de Physicochimie des Solutions, E.N.S.C.P., 11 Rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

CHRISTIAN BELLEC
Laboratoire de Chimie des Hétérocycles, Université Pierre et Marie Curie, 4, Place Jussieu, 75230 Paris Cedex 05, France

AND

JEAN PINSON
Laboratoire d'Electrochimie, Université Paris VII, 2, Place Jussieu, 75231 Paris Cedex 05, France

Received May 7, 1982

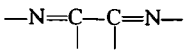
JOSEPH ARMAND, LINE BOULARES, CHRISTIAN BELLEC, and JEAN PINSON. Can. J. Chem. **60**, 2797 (1982).

The electrochemical reduction of quinoxalino[2,3-*b*]quinoxaline gives fluoflavine (**2**) the structure of which is discussed. The electrochemical reduction of fluoflavine in acidic medium leads to a hexahydroquinoxalino[2,3-*b*]quinoxaline. A reduction mechanism is proposed based on cyclic voltammetry results and preparative electrolysis. The results obtained in the case of quinoxalino[2,3-*b*]quinoxaline are used to rationalize the results obtained in the case of pyrazino[2,3-*b*]pyrazines and pyrazino[2,3-*b*]quinoxalines.

JOSEPH ARMAND, LINE BOULARES, CHRISTIAN BELLEC et JEAN PINSON. Can. J. Chem. **60**, 2797 (1982).

La réduction électrochimique de la quinoxalino[2,3-*b*]quinoxaline fournit la fluoflavine (**2**) dont la structure est discutée. La réduction électrochimique de la fluoflavine en milieu acide fournit une hexahydroquinoxalino[2,3-*b*] quinoxaline. Un mécanisme de réduction utilisant les résultats de la voltammétrie cyclique et des électrolyses préparatives est proposé. La présente étude permet également de rationaliser certains résultats obtenus dans des études antérieures relatives aux pyrazino[2,3-*b*] pyrazines et pyrazino[2,3-*b*] quinoxalines.

We have been interested for some time in the electrochemical reduction of heterocyclic compounds with two 1,4-nitrogen atoms in a six-membered ring. We now report the electrochemical reduction in protic and aprotic medium of the quinoxalino[2,3-*b*]quinoxaline, **1**. This compound possesses two conjugated

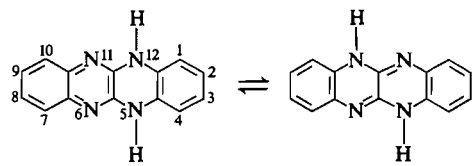


systems and it seemed interesting to investigate how the conjugation of two such systems would influence their electrochemical behaviour. A single electrochemical study of **1** has been published (1); however, its conclusions are erroneous.

As we shall see later on, the electrochemical reduction of the quinoxalino[2,3-*b*]quinoxaline **1** leads to fluoflavine which is a dihydro quinoxalino-[2,3-*b*]quinoxaline. It can also be prepared by condensation of 2,3-dichloroquinoxaline with *o*-phenylene diamine (2). The structure of fluoflavine has remained controversial as some authors assigned a 5,12-dihydro structure **2** (3), while others assigned a 5,11-dihydro structure **2***a* (2). Therefore, we shall first discuss the structure of fluoflavine.

The structure of fluoflavine

Some of the problems arising in the investigation of the structure of this compound stem from its very low solubility in usual solvents (methanol, acetonitrile, dimethylsulphoxide, dimethylformamide). It can be dissolved in hot acetic acid or in cold trifluoroacetic acid. Our first attempts aimed at obtaining an unambiguous determination of the structure by X-ray crystallography, but we were unable to obtain suitable crystals from CH_3COOH or CF_3COOH solutions. An nmr spectrum recorded in CF_3COOH shows a single AA'BB' pattern for the eight aromatic protons, which gives no indication on the structure of fluoflavine the protons of the benzenic rings being equivalent because of the protonation of the nitrogen atoms and the fast exchange of these protons.

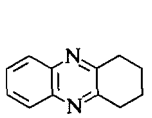


2 **2***a*

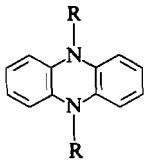
An nmr spectrum of fluoflavine in Me_2SO-d_6 obtained on a 250 MHz spectrometer after 3000 accumulations shows two aromatic multiplets located respectively at 6.45–6.75 ppm (4H) and 6.90–7.13 ppm (4H) and a broad signal at 9.92 ppm corresponding to the two NH protons. This spectrum rules out the existence of a fast equilibrium

0008-4042/82/222797-07$01.00/0

between the tautomers **2** and **2***a* because the aromatic protons of the two benzenic rings would be equivalent and the spectrum would consist of a single AA'BB' pattern, the width of which can be estimated to about 0.15 ppm (the aromatic protons of 5,10-dihydro-2,3-dimethyl-pyrazino[2,3-*b*]quinoxaline appear as an AA'BB' pattern with a width of 0.12 ppm). Thus, fluoflavine has either structure **2** or structure **2***a*. Structure **2** should give rise to two separated AA'BB' patterns. The aromatic protons of 1,2,3,4-tetrahydrophenazine **3** appear as a multiplet between 7.50 and 8.10 ppm (4) while that of 5,10-bis-*n*-propyl-5,10-dihydrophenazine **4** appear



3



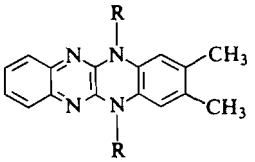
4 R = *n*-propyl

between 6.06 and 6.70 ppm (5). Thus, the observed spectrum is in agreement with structure **2**, but its poor resolution does not permit the measurement of the characteristics of the two possible AA'BB' patterns. This is why it is not possible to rule out structure **2***a* which could also evidence two multiplets of equal intensity. By heating fluoflavine in acetic anhydride a single diacetyl derivative **25** is obtained. Its 250 MHz nmr spectrum shows two aromatic AA'BB' patterns which proves that **25** is a 5,12-diacetylated derivative. The structure of **25** is confirmed by its electrochemical reduction (vide infra) which gives *N*,*N*'-diacetyl *o*-phenylene diamine. Obtaining a single diacetyl derivative in the 5,12-positions is in agreement with structure **2** but does not allow the exclusion of structure **2***a*; indeed, it is possible that at high temperature the **2***a* → **2** interconversion be faster than the acetylation of **2**.

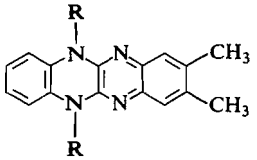
We have shown previously (8) that the electrochemical reduction of the pyrazino[2,3-*b*]quinoxaline **18** leads to the only 5,10-dihydro derivative **20**, **18** and **20** forming a redox couple (see Scheme 4). As we shall see further the electrochemical reduction of **1** only gives fluoflavine and **1** and fluoflavine also form a redox couple. As **1** and **18** have very similar structures this result favours structure **2** for fluoflavine.

It should also be remarked that the condensation of 2,3-dichloroquinoxaline with 1,2-diamino-4,5-dimethylbenzene gives a solid which by heating in acetic anhydride leads to a mixture of the 5,12-diacetyl-5,12-dihydro derivative **7** and of the 6,11-diacetyl-6,11-dihydro derivative **8**. This result points to the formation of a mixture of the 5,12-dihydro derivative **5** and of a 6,11-dihydro derivative **6** upon condensation. As the influence of the methyl groups on the structure of a dihydroquinoxalino[2,3-*b*]quinoxaline is most likely very small, the structures of **5** and **6** support structure **2** for fluoflavine.

Thus, although there is no formal proof that fluoflavine has structure **2**, the above results show structure **2** as the most likely; thus it will be used in this paper.



5, R = H
7, R = $COCH_3$



6, R = H
8, R = $COCH_3$

Electrochemical reduction of quinoxalino[2,3-b]-quinoxaline

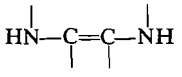
In aprotic medium (CH_3CN) a voltammogram of **1** presents two reversible peaks at $E_1^0 = -0.37$ V and $E_2^0 = -1.05$ V which correspond to the formation of a radical anion and a dianion.

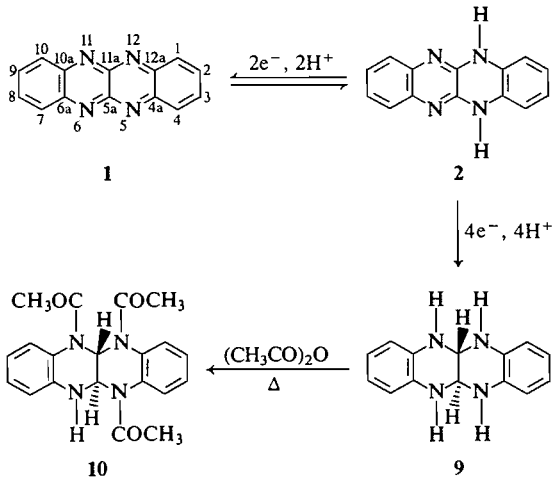
In hydroorganic medium (50/50 v/v water–dimethylformamide) **1** presents a 2F wave which is pH dependent between pH 4 and 12: $E_{1/2}$ (V) = 0.44 − 0.058pH; **1** is unstable in more acidic or more basic media. Between pH 4 and 6, this first wave is followed by a pH-dependent 4F wave: $E_{1/2}$ (V) = −0.75 − 0.068pH; above pH 6 the height of the second wave decreases and disappears at pH > 8.

A preparative electrolysis of **1** on the first plateau gives **2**. The second 4F wave is that of **2**. The electrochemical reduction of **2** in acidic medium where it is slightly more soluble leads to 5,5a,6,11,-11a,12-hexahydroquinoxalino[2,3-*b*]quinoxaline, **9**. When **9** is heated in acetic anhydride, it furnishes a triacetyl derivative **10**. The large value of the $^3J_{5a-11a}$ coupling constant (18 Hz) of **10** points to a *trans* configuration for the hydrogens 5a and 11a. The results are summarized in Scheme 1.

The results of a previous polarographic study of **1** (1) are erroneous as the authors do not mention the first wave of **1** and assign the second wave to **1** instead of **2**. Besides, no preparative electrolysis is described.

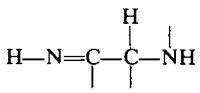
Concerning the reduction mechanism, the formation of **2** from **1** is in agreement with what could be expected from the known reduction of compounds with a pyrazine ring. Pyrazines (9), quinoxalines (10), and pyrido[2,3-*b*]pyrazines (11) are first reduced to compounds with a



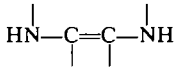


SCHEME 1

structure. The same reaction is observed for the reduction of **1** into **2**. But unlike previous compounds which rearrange to



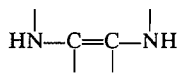
structures the



structure of **2** is stable. This is obviously related to the increased number of conjugated cycles.

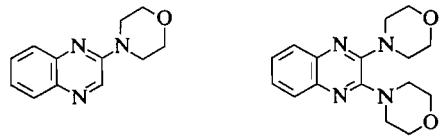
In the case of **2**, one could expect for the same reasons as above the primary formation of a 5,6,11,12-tetrahydrogenated compound **11** which would rearrange to a 5,5a,6,12-tetrahydrogenated compound **12**, the reduction of which would lead to a hexahydrogenated compound such as **9** (Scheme 3).

Compounds such as **11** with a

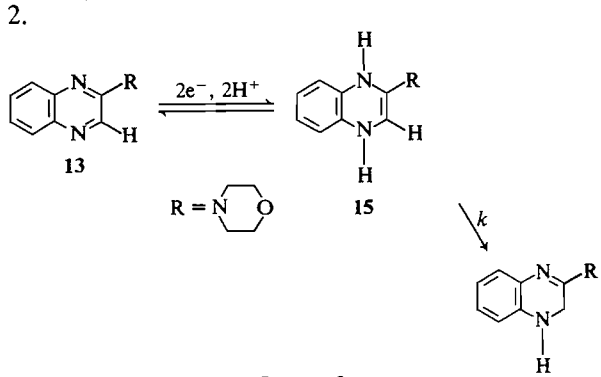


structure are usually characterized by an anodic peak on their voltammogram. The potential of this anodic peak is generally near or identical to that of the cathodic peak of the parent heterocycle (see, e.g., 2-phenylquinoxaline (10), 2,3-diphenylpyrazine (9), diphenylpyrido[3,4-*b*]pyrazine (11)). No anodic peak which could correspond to **11** can be observed on mercury, but on a glassy carbon electrode, an anodic peak II_a appears at E_{pa} = +0.65 V if the cathodic peak of fluoflavine II_c (E_{pc} = −0.93 V) has been scanned before (Fig. 1, v = 0.2 V s^{-1}, pH 1, 50% DMF), the reversible couple which appears at E^0 = +0.45 V, I_c/I_a being that of fluoflavine itself.

In order to find out the origin of the large positive shift of the anodic peak we investigated the behaviour of 2-morpholinoquinoxaline **13** where the pyrazine ring also bears a nitrogen substituent.

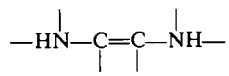


In hydroorganic medium (50/50 v/v methanol–water) **13** presents a 2F cathodic wave (1 < pH < 4.5: $E_{1/2}$ = −0.15 − 0.11 pH and 4.5 < pH < 13: $E_{1/2}$ = −0.39 − 0.061 pH). Its electrolysis in basic medium furnishes the 3,4-dihydro-2-morpholinoquinoxaline and its cyclic voltammetry in basic medium (25% DMF, 0.1 *N* NaOH, v = 20 V s^{-1}) shows a cathodic peak at E_{pc} = −1.50 V and an anodic peak at E_{pa} = −0.88 V. Thus in basic media 2-morpholinoquinoxaline presents a voltammetric behaviour similar to the other quinoxalines already investigated. Its reduction is summarized in Scheme 2.

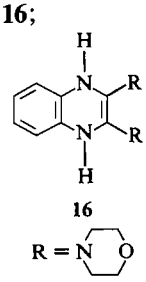


SCHEME 2

In acidic medium under the same conditions as fluoflavine (v = 0.2 V s^{-1}, pH = 1, 50% DMF) the cathodic peak of **13** is observed at E_{pc} = −0.50 V and the anodic peak corresponding to the



structure **15** appears at E_{pa} = +0.73 V. In the same way 2,3-dimorpholinoquinoxaline **14** gives under the same conditions a cathodic peak at E_{pc} = −0.93 V and an anodic peak at E_{pa} = +0.78 V corresponding to **16**;



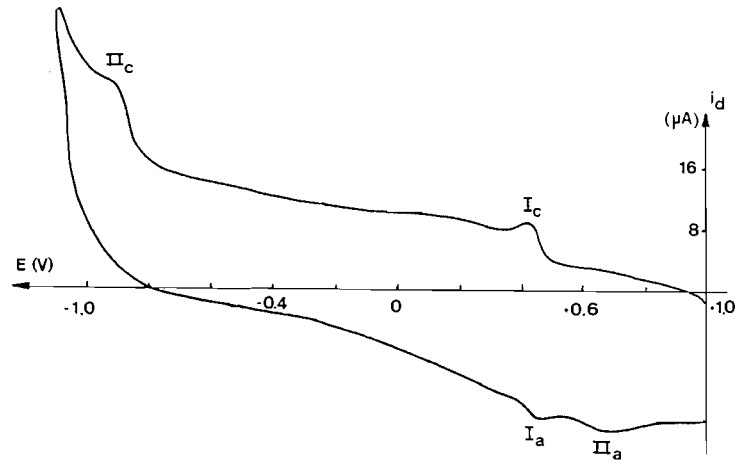
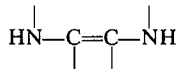
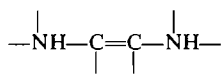


FIG. 1. Voltammogram of fluoflavin **2** at pH 1; 50% DMF; $v = 0.2\,V\,s^{-1}$.

Thus, it appears that in the case of

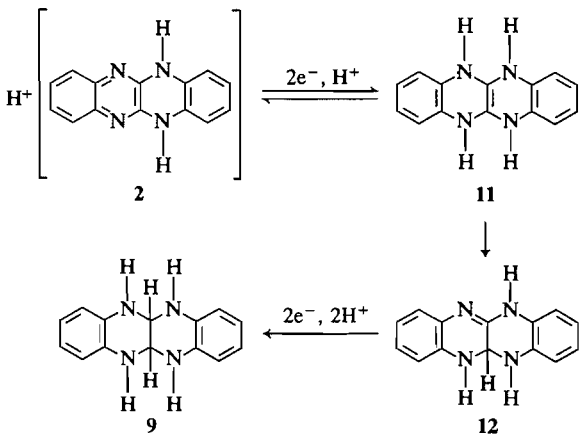


structures substituted by amino groups on the two central atoms their anodic peak is shifted to positive potentials in acidic medium. This can be related to the protonation of the amino substituents. The protonated amino groups are strongly electron-withdrawing making the reoxidation of the



system more difficult. This can also be confirmed with the diacetyl derivative of fluoflavine **25** (Scheme 5) which gives a 2F cathodic peak at $E_{pc} = -0.51\,V$ and an anodic peak at $E_{pa} = -0.31\,V$ ($v = 0.2\,V\,s^{-1}$, pH 1, 50% DMF). Indeed in the case of **25** the two substituted amino groups remain unprotonated.

Scheme 3 can be proposed for the reduction of

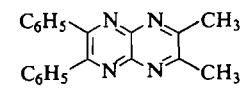


SCHEME 3

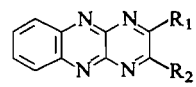
fluoflavine. It is not possible to accurately measure the rate of rearrangement of **11** to **12** as the cathodic wave of fluoflavine merges in the background discharge upon increasing the sweep rate, but its order of magnitude can be estimated to about 0.2 s^{-1} from the peaks height.

Electrochemical reduction of pyrazino[2,3-b]-pyrazines and pyrazino[2,3-b]quinoxalines

Let us now turn back to the reduction of less conjugated systems such as pyrazino[2,3-*b*]pyrazines **17** and pyrazino[2,3-*b*]quinoxalines **18**. In the

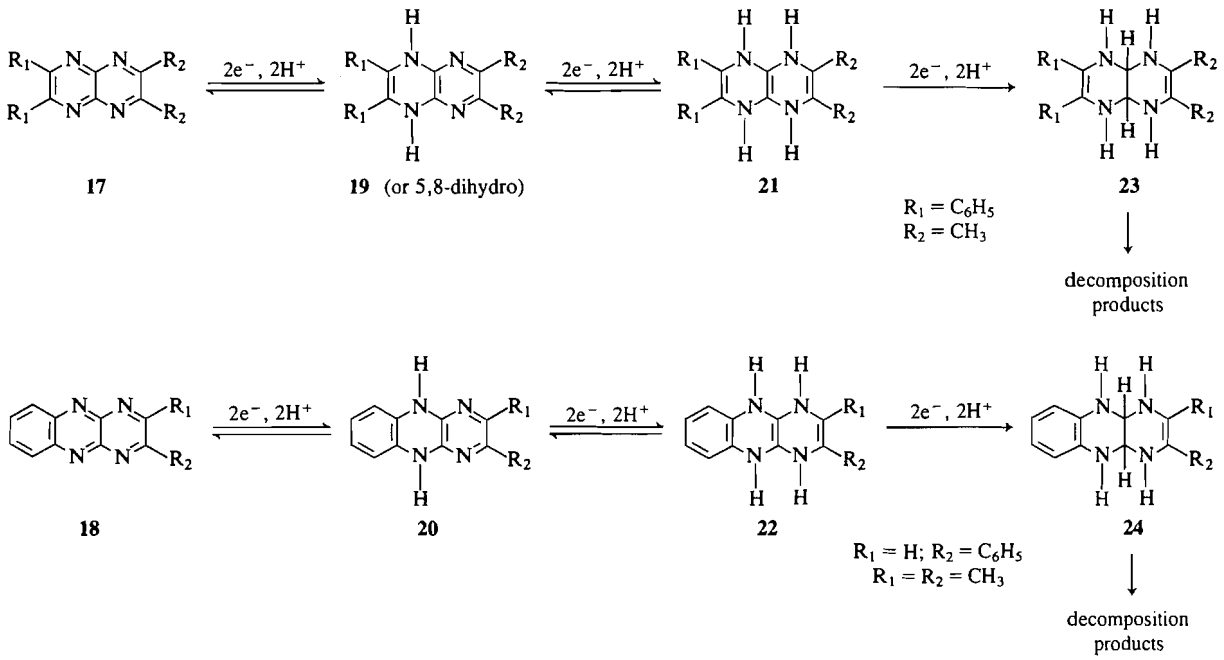


17



18

case of **17** one observes a 2F wave corresponding to the formation of a 1,4- (or 5,8-) dihydroderivative **19**, followed by a 4F wave in acidic medium. In the same way **18** presents a 2F wave corresponding to the formation of a 5,10-dihydroderivative **20** (8) followed by a 4F wave in acidic medium (7). In both cases preparative electrolysis at the level of the second plateau lead to gummy products from which no defined product could be characterized. A cyclic voltammogram of **17** ($v = 0.2\,V\,s^{-1}$, glassy carbon electrode, pH = 4.3, 50% DMF) presents a cathodic peak at $E_{pc} = -0.50\,V$ and an anodic peak at $E_{pa} = -0.26\,V$ corresponding to the **17/19** couple. A second cathodic peak is observed at $-1.16\,V$. If one scans at potentials more negative than this second peak at $v = 50\,V\,s^{-1}$ an anodic peak appears at $+0.59\,V$ which can be assigned to **21** by comparison with the voltammograms of **2**, **13**, and **14**. The same kind of voltammogram is observed in the case of **18** where an anodic peak appears at $+0.63\,V$ ($v = 0.2\,V\,s^{-1}$) if the second cathodic peak has been



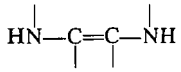
SCHEME 4

scanned beforehand. Scheme 4 can be proposed for the reduction of **17** and **18**. The instability of **23** and **24** is most likely related to their enediamine structure, while **9** which possesses a structure similar to that of *o*-phenylene diamine is stable.

Electrochemical reduction of 5,12-diacetyl-5,12-dihydroquinoxalino[2,3-b]quinoxaline 25

When heated in acetic anhydride, **2** furnishes **25** which is more soluble than **2** in the usual solvents. In CH_3CN, the voltammogram of **25** presents a first monoelectronic cathodic peak at $E_{pc1} = -1.5$ V followed by a bielectronic peak at $E_{pc2} = -2.35$ V (at 0.2 V s^{-1}). The first peak corresponds to the formation of the radical anion, while an electrolysis at the level of the second peak mainly gives fluoflavine.

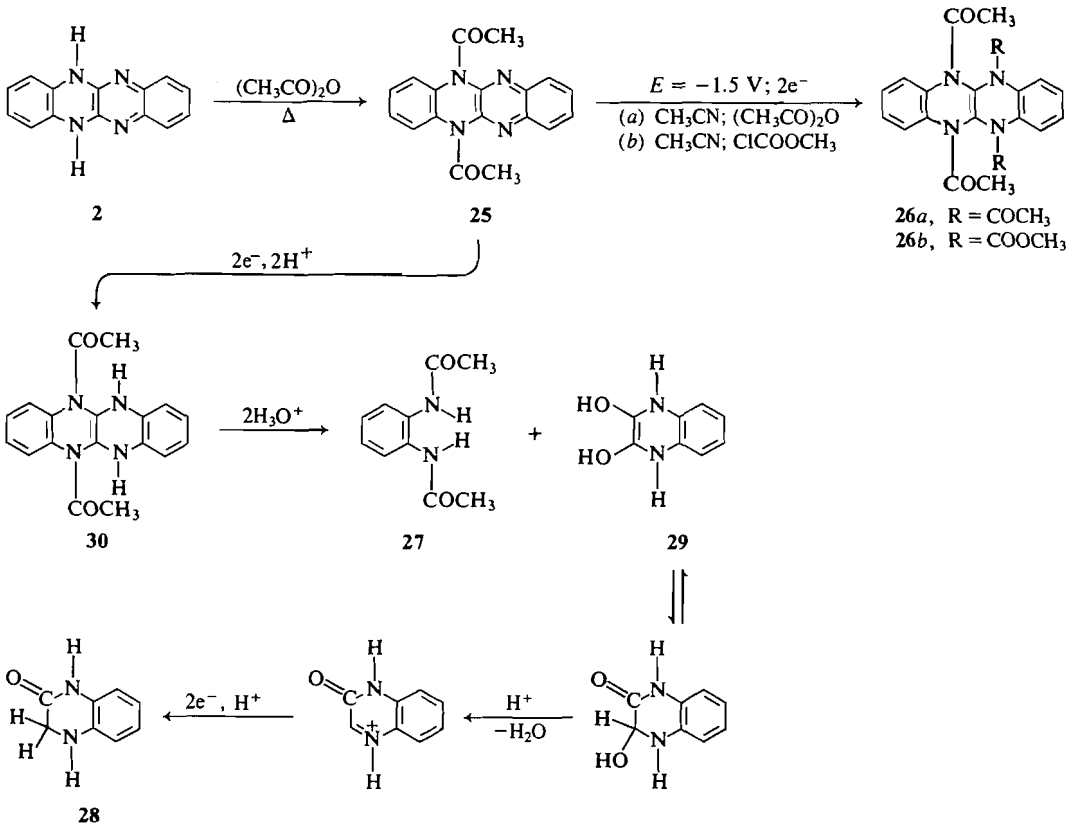
An electrolysis of **25** in CH_3CN in the presence of acetic anhydride gives the 5,6,11,12-tetraacetylated-5,6,11,12-tetrahydro derivative **26***a* (Scheme 5). In the presence of methylchloroformate the 5,6-diacetyl-11,12-dicarbomethoxy-5,6,11,12-tetrahydro derivative **26***b* is obtained. In hydroorganic medium (CH_3CN–H_2O; 50/50 v/v), **25** shows a 2F polarographic wave which is pH dependent, $E_{1/2}$ (V) = −0.37 − 0.08 pH. An electrolysis of a 10^{-3} *M* solution gives an oxidizable compound with a 2F anodic wave at a potential near that of the cathodic wave of **25**. At pH 1.5 this reduction compound gives a product more easily reduced than **25** so that 4F/mol are consumed during the electrolysis. A preparative electrolysis gives a mixture of *N*,*N*′-diacetyl orthophenylenediamine **27** and 1,2,3,4-tetrahydroquinoxaline-2-one **28**. It has been shown previously (12, 13) that the 2,3-dihydroxyquinoxaline **29** leads to **28** by electrochemical reduction, thus the formation of **27** and **28** from **25** should follow the reaction path described in Scheme 5. The primary reduction product responsible for the anodic wave on the voltammogram of **25** would be 5,6-diacetyl-5,6,11,12-tetrahydroquinoxalino[2,3-*b*]quinoxaline **30**, in agreement with a



structure described above. The formation of **30** is also supported by the formation of **26** when the reduction is carried out in the presence of acetic anhydride. **30** would be hydrolyzed in acidic medium into **27** and **29**, the latter compound leading to **28**.

Experimental section

Melting points are uncorrected. ^{1}H-nmr spectra were recorded on a Bruker WH 80, a Varian A 60, and a Bruker 250 MHz spectrometer, using tetramethylsilane (TMS) as internal standard. The apparatus and techniques used for the electrochemical studies and pH measurements have been described previously (11). All the potentials are referred to the saturated calomel electrode (sce); the temperature of the solutions was 20°C. The microanalyses were performed by the "Service de Microanalyse-Université Pierre et Marie Curie". The following abbreviations are used in reporting nmr results: s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet.



SCHEME 5

Preparation of 1 and 2

Quinoxalino[2,3-*b*]quinoxaline **1** was prepared from 5,12-dihydroquinoxalino[2,3-*b*]quinoxaline **2** (fluoflavine) according to ref. 14. Compound **2** was obtained (2) by condensation of *o*-phenylenediamine with 2,3-dichloroquinoxaline.

*5,12-Diacetyl-5,12-dihydroquinoxalino[2,3-*b*]quinoxaline, 25*

A suspension of 500 mg of **2** in 25 mL of acetic anhydride was refluxed for 24 h. Acetic anhydride was evaporated and the residue was crystallized from ethylacetate; 400 mg; mp 202–203°C. ^{1}H-nmr ($CDCl_3$, 250 MHz): 5-CH_3CO and 12-CH_3CO, s, 2.59 ppm (6H); 1-H, 2-H, 3-H, 4-H, AA'BB' pattern at 7.34 ppm, m (2H) and 7.94 ppm, m (2H); 7-H, 8-H, 9-H, 10-H, AA'BB' pattern at 7.82 ppm, m (2H) and 8.27 ppm, m (2H). *Anal.* calcd. for $C_{18}H_{14}N_4O_2$: C 67.91, H 4.43, N 17.60; found: C 67.85, H 4.51, N 17.56.

*Preparation of 5,12-diacetyl-5,12-dihydro-2,3-dimethylquinoxalino[2,3-*b*]quinoxaline, 7, and 6,11-diacetyl-6,11-dihydro-2,3-dimethylquinoxalino[2,3-*b*]quinoxaline, 8*

A mixture of 5 g of 2,3-dichloroquinoxaline and 6.8 g of 2,3-diamino-5,6-dimethylbenzene in 50 mL of ethyleneglycol was refluxed for 45 min. The cooled reaction mixture was filtered, washed with dimethylformamide and ethanol to give 5.2 g of a yellow–orange solid. This solid (500 mg) was then refluxed in 25 mL of acetic anhydride for 2 h. Acetic anhydride was evaporated and the residue was filtered, washed with water, and dried to give 590 mg of a mixture of **7** and **8** as shown by nmr. Compound **7** is less soluble in ethylacetate than **8**, the two products have been obtained pure after several crystallizations. **7**: mp 210°C, ^{1}H-nmr ($CDCl_3$): 2-CH_3, 3-CH_3, 5-$COCH_3$, 12-$COCH_3$, 2.27 and 2.53 ppm, two s (2 × 3H); 1-H, 4-H, 7.50 ppm, s (2H); 7-H, 8-H, 9-H, 10-H, AA'BB' pattern, 7.60–8.15 ppm, m (4H). *Anal.* calcd. for $C_{20}H_{18}N_4O_2$: C 69.35, H 5.24, N 16.18; found: C 69.29, H 5.28, N 16.22. **8**: mp 215°C; ^{1}H-nmr ($CDCl_3$): 2-CH_3, 3-CH_3, 6-$COCH_3$, 11-$COCH_3$, 2.50 ppm and 2.55 ppm, two s (2 × 3H); 1-H, 4-H, 7.72 ppm, s (2H); 7-H, 8-H, 9-H, 10-H, AA'BB' pattern at 7.23 ppm, m (2H) and 7.84 ppm, m (2H). *Anal.* calcd. for $C_{20}H_{18}N_4O_2$: C 69.35, H 5.24, N 16.18; found: C 69.48, H 5.19, N 16.09.

Electrolysis of 1 in hydroorganic medium: preparation of 2

An electrolysis was carried out at pH 6.75 and $E = -0.5$ V (sce). The cathodic compartment contained 100 mg of **1** in 200 mL of solution (dimethylformamide 50%). At the end of the electrolysis (2F per mol) the precipitate in the cell was filtered, washed with water and ethanol, then dried to give 95 mg of 5,12-dihydroquinoxalino[2,3-*b*]quinoxaline **2**.

Electrolysis of 2 in hydroorganic medium: preparation of 9

An electrolysis was carried out using 800 mg of **2** partially dissolved in 200 mL of solution (50% CH_3CN; 1 *N* H_2SO_4) at $E = -0.9$ V. At the end of the electrolysis (4.2 F per mol), acetonitrile was evaporated and the solution was neutralized with 2 *N* NaOH. The solid precipitated was filtered, washed with water, and dried to give 570 mg of 5,5a,6,11,11a,12-hexahydroquinoxalino[2,3-*b*]quinoxaline **9**, mp 270–275°C dec.[1]

[1]The solid state structure and the solution conformations of **9** are presently under investigation. This compound has a structure analogous to 1,4,5,8-tetraazadecalin (TAD) systems which have been the subject of recent sustained interest, see e.g., ref. 6.

^{1}H-nmr (DMSO-d_6): 5-H, 6-H, 11-H, 12-H, 4.45 ppm, m (2H) and 5.22 ppm, m (2H) exchanged with D_2O; 5a-H, 11a-H, 4.57 ppm, s (2H); 1-H, 2-H, 3-H, 4-H, 7-H, 8-H, 9-H, 10-H, 6.5 ppm, m (4H) and AA'BB' pattern centered at 7.32 ppm (4H). *Anal.* calcd. for $C_{14}H_{14}N_4$: C 70.56, H 5.92, N 23.51; found: C 70.64, H 6.01, N 23.35.

Acetylation of 9: preparation of 10

A solution of 650 mg of **9** in 5 mL of acetic anhydride was refluxed for 15 h, cooled at 0°C. The solid precipitated was filtered, washed with water, and dried to give 360 mg of 5,6,11-triacetyl-5,5a,6,11,11a,12-hexahydroquinoxalino[2,3-*b*]quinoxaline **10**, mp 222–223°C. ^{1}H-nmr ($CDCl_3$): 5-$COCH_3$, 6-$COCH_3$, 11-$COCH_3$, three singlets at 1.90, 2.45, and 2.80 ppm (3 × 3H); 5a-H, 11a-H, two d at 4.56 ppm and 5.98 ppm, J_{5a-11a} = 18 Hz; 1-H, 2-H, 3-H, 4-H, 7-H, 8-H, 9-H, 10-H, m, 7.1–8.4 ppm (8H); 12-H, broad s, 9.87 ppm (1H) exchanged with D_2O. *Anal.* calcd. for $C_{20}H_{20}N_4O_3$: C 65.92, H 5.53, N 15.38; found: C 66.07, H 5.56, N 15.30.

Electrolysis of 25 in acetonitrile

The cathodic solution contained 60 mL of solvent, 580 mg of **25**, and 6 g of tetrabutylammonium iodide; $E = -2.4$ V. At the end of the electrolysis (2.1F per mol) the solution was poured into 200 mL of water and the solid precipitated was filtered, washed with water, and dried to give 200 mg of **2**.

*Electrolysis of 25 in acetonitrile in the presence of acetic anhydride: preparation of 26*a

The cathodic solution contained 60 mL of solvent, 800 mg of **25**, 8 mL of acetic anhydride, and 6 g of tetrabutylammonium iodide; $E = -1.5$ V. A solid precipitated during the electrolysis. At the end, the precipitate was filtered, washed with water and acetonitrile, and dried to give 200 mg of 5,6,11,12-tetraacetyl-5,6,11,12-tetrahydroquinoxalino[2,3-*b*]quinoxaline ***26a***, mp > 300°C. ^{1}H-nmr (TFA): 5-$COCH_3$, 6-$COCH_3$, 11-$COCH_3$, 12-$COCH_3$, s, 2.50 ppm (12H); 1-H, 2-H, 3-H, 4-H, 7-H, 8-H, 9-H, 10-H, m, 7.4–8.0 ppm (8H). *Anal.* calcd. for $C_{22}H_{20}N_4O_4$: C 65.33, H 4.99, N 13.86; found: C 65.26, H 5.04, N 13.97.

*Electrolysis of 25 in acetonitrile in the presence of methylchloroformate: preparation of 26*b

The cathodic solution contained 60 mL of solvent, 800 mg of **25**, and 6 ml of methylchloroformate and 6 g of tetrabutylammonium iodide; $E = -1.5$ V. At the end of the electrolysis ($i < 3$ mA) the catholyte was poured into 250 mL of water. The solid precipitated was filtered, washed with water, and dried to give 690 mg of 5,12-diacetyl-6,11-dicarbomethoxy-5,6,11,12-tetrahydroquinoxalino[2,3-*b*]quinoxaline, ***26b***, mp 294°C. ^{1}H-nmr (TFA): 5-$COCH_3$, 12-$COCH_3$, s, 2.50 ppm (6H); 6-$COOCH_3$, 11-$COOCH_3$, s, 4.0 ppm (6H); 1-H, 2-H, 3-H, 4-H, 7-H, 8-H, 9-H, 10-H, m, 7.3–8.0 ppm (8H). *Anal.* calcd. for $C_{22}H_{20}N_4O_6$: C 60.54, H 4.62, N 12.84; found: C 60.61, H 4.64, N 12.93.

Electrolysis of 25 in hydroorganic medium

Electrolysis was carried out with 800 mg of **25** in 200 mL of solution (50% CH_3CN; 0.1 *N* H_2SO_4); $E = -0.7$ V. At the end of the electrolysis (4F per mol) acetonitrile was evaporated. The solution was neutralized with solid $NaHCO_3$ and extracted three times with 60 mL of chloroform. The organic layer was dried with Na_2SO_4 and evaporated to give 300 mg of a solid which was shown by nmr to be a mixture of *N*,*N'*-diacetylorthophenylenediamine **27** and 1,2,3,4-tetrahydroquinoxaline-2-one **28**. Compound **27** is soluble in ethyl acetate, contrary to **28**. This allows the separation of products which were both identified with authentic samples: **27** (15) and **28** (16).

Preparation of 2-morpholinoquinoxaline 13 and 2,3-dimorpholinoquinoxaline 14

Compound **13** was prepared according to ref. 17. 2,3-Dimorpholinoquinoxaline **14** was obtained by heating 2,3-dichloroquinoxaline (5 g) and morpholine (15 mL) in a stainless steel vessel for 24 h at 140°C. The solid obtained was poured into 200 mL of water, filtered, and crystallized in $CHCl_3/CH_3OH$; 80/20, v/v; 3.6 g, mp 223°C. ^{1}H-nmr (TFA): 5-H, 6-H, 7-H, 8-H, AA'BB' pattern at 7.6–8.1 ppm (4H); CH_2 of morpholine ring, m at 3.8–4.5 ppm (16H). *Anal.* calcd. for $C_{16}H_{20}N_4O_2$: C 63.98, H 6.71, N 18.65; found: C 64.07, H 6.66, N 18.87.

Electrolysis of 2-morpholinoquinoxaline 13 in hydroorganic medium

13 (560 mg) was dissolved in 100 mL of solution (50% CH_3OH, NaOH 0.1 *N*) and electrolyzed at −1.4 V. After consumption of about 2F per mol the methanol was evaporated and the solution was extracted with ether. The ethereal extracts were evaporated. The residual oil was dried over P_2O_5 to give 320 mg of an hygroscopic solid: 3,4-dihydro-2-morpholinoquinoxaline, mp = 90°C dec. ^{1}H-nmr ($CDCl_3$ + D_2O): CH_2 of morpholine ring, m, 3.3–3.8 ppm (8H); 3-CH_2, s, 3.92 ppm (2H); 5-H, 6-H, 7-H, 8-H, m, 6.4–7.2 ppm (4H). *Anal.* calcd. for $C_{16}H_{22}N_4O_2$: C 63.55, H 7.30, N 18.53; found: C 63.47, H 7.38, N 18.52.

1. P. O. Kosonen and R. Gustafsson. Finn. Chem. Lett. 204 (1977).
2. S. Hunig, D. Scheutzow, H. Schlaf, and H. Quast. Liebig's Ann. **765**, 110 (1972).
3. G. M. Badger and P. J. Nelson. Aust. J. Chem. **16**, 445 (1963).
4. J. Stating, S. Reiffers, and H. Wynberg. Synthesis, 211 (1971).
5. G. F. Bettinetti, S. Maffei, and S. Pietra. Synthesis, 748 (1976).
6. (*a*) B. Fuchs, S. Weinman, U. Shmuelli, A. R. Katritzky, and R. C. Patel. Tetrahedron Lett. **22**, 354 (1981); (*b*) J. Jazwinski and R. A. Kolinski. Tetrahedron Lett. **22**, 1711 (1981).
7. J. Armand, K. Chekir, and J. Pinson. C.R. Acad. Sci. Ser. C, **284**, 391 (1977).
8. J. Armand, L. Boulares, K. Chekir, and Ch. Bellec. Can. J. Chem. **59**, 3237 (1981).
9. J. Armand, K. Chekir, and J. Pinson. Can. J. Chem. **52**, 3971 (1974).
10. J. Pinson and J. Armand. Coll. Czech. Chem. Commun. **36**, 585 (1971).
11. J. Armand, K. Chekir, and J. Pinson. Can. J. Chem. **56**, 1804 (1978).
12. J. Armand, Y. Armand, and L. Boulares. C.R. Acad. Sci. Ser. C, **286**, 17 (1978); Journées d'Electrochimie, Tours, France. (1978).
13. R. Gottlieb and W. Pfleiderer. Chem. Ber. **111**, 1753 (1978).
14. W. Ried and P. Schäfer. Chem. Ber. **103**, 2225 (1970).
15. K. J. Morgan and A. M. Turner. Tetrahedron, **22**, 1175 (1966).
16. J. Ploechl. Chem. Ber. **19**, 6 (1886).
17. G. W. Cheeseman. J. Chem. Soc. 3236 (1957).