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The electrochemical reduction of cinoxacin (I) has resulted, *via* a series of chemical and electrochemical steps, in the formation of an indole dione III.

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In an effort to determine the absolute purity of cinoxacin (I), an antibacterial agent useful in treating urinary tract infections (1), an electrochemical reduction under controlled potential coulometric conditions (2,3) at a stirred mercury pool electrode was carried out. The reduction has resulted, *via* a series of chemical and electrochemical steps, in the unexpected formation of the isatin derivative III.

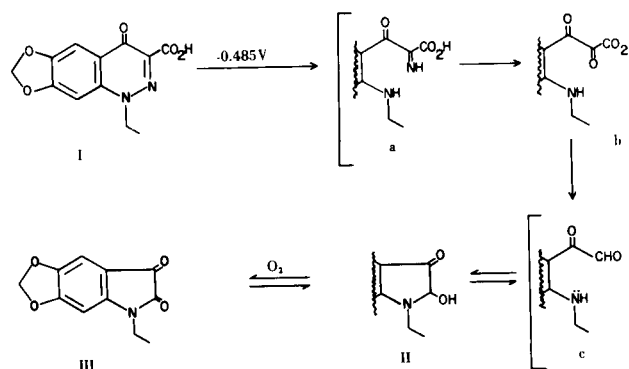
Scheme I presents our rationale for this rearrangement. The initial electrochemical process involves a $2e^-$ reduction of the N-N bond (4,5) to afford species *a*. Controlled potential coulometry confirms the quantitative transfer of $2e^-$ in this reduction step. [In acidic media, the N-N bond has been shown to be more easily reduced than the C=N bond in compounds containing the C=N-N moiety (6)]. The cathodic shift in the polarographic half-wave potential with increasing *pH* and the shape of the polarographic wave indicate that chemical reactions are associated with the electron transfer. Data from cyclic voltammetric experiments demonstrate that the time scale of these initial chemical reactions is several milliseconds in typical aqueous supporting electrolytes.

At longer times, additional chemical rearrangements (hydrolysis to *b*, decarboxylation to *c*, cyclization to II and finally oxidation) lead to the formation of a reddish-brown product which has been isolated and characterized as dione III. This product is also electroactive. At the electrolysis potential employed for the initial reduction of cinoxacin, the substituted dione is held in reduced form II which spontaneously oxidizes to III when the electrolysis is halted. The redox couple is polarographically reversible and controlled potential coulometry indicates that II \rightarrow III is a $2e^-$ process.

The literature (6) does contain examples of electrochemical processes involving hydrolysis (IV \rightarrow V) or ring closure with ring contraction (VI \rightarrow VII). However, this

appears to be the first instance of an electrochemical ring closure with ring contraction to form an indole dione.

Scheme 1



EXPERIMENTAL

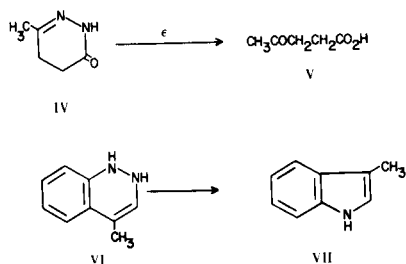
5-Ethyl-5H-1,3-dioxolo[4,5-*f*]indole-6,7-dione (III).

A solution of 0.26 g. (20 mmoles) of I in 50 ml. of 1/1 water-formic acid was reduced at a stirred mercury pool electrode at -0.65V vs a saturated calomel reference electrode. The initial fluorescent greenish-yellow solution turns to red-brown after the electrolysis is discontinued. The solution is next diluted with water and then extracted with chloroform. The chloroform is dried and evaporated to give 0.20 g. (92%) of dark solids. Two recrystallizations from methanol afford red-brown crystalline analytical material which sublimes at 150°, 0.1 mm Hg; ir (potassium bromide): 1745, 1720 cm^{-1} (strong, C=O), 1620 (C=C); *cf.* *N*-methylisatin (7) 1750, 1730, 1620 cm^{-1} ; nmr (deuteriochloroform): 7.0 δ (s, 1H, H₈), 6.5 (s, 1H, H₄), 6.1 (s, 2H, -CH₂-), 3.7 (q, 2H, CH₃CH₂-), 1.3 (t, 3H, CH₃-); uv (5% methanol): 204 nm (log ϵ 4.09), 276 (4.27), 328.5 (3.69) 385 (2.92); *cf.*, isatin 208 (4.12), 242 (4.33), 302 (3.55), 420 (2.82); ms: *m/e* 219 (M⁺), major fragments at *m/e* 191 (M⁺-C=O), 176 (M⁺-NCH₂CH₃), 163 (M⁺-COCO); exact mass (219.0529), calculated for C₁₁H₉NO₄, 219.0531.

Anal. Calcd. for C₁₁H₉NO₄: C, 60.28; H, 4.14; N, 6.39. Found: C, 60.25; H, 4.41; N, 6.40.

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