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# A SELECTIVE CATHODIC REDUCTION OF β-CHLOROVINYLIMINES IN N, N' DIMETHYLFORMAMIDE

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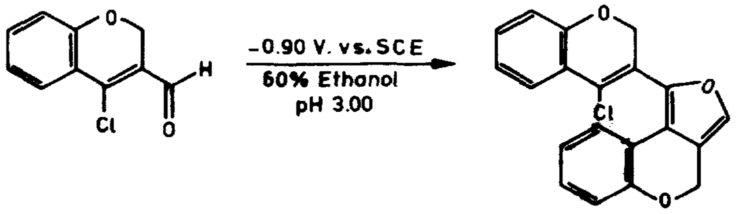
## ABSTRACT

The controlled-potential electrolyses of various subsituted chlorovinylimines, viz., 4-chloro-3-(N-aryliminomethyl)-2H(1)-benzopyrans in dimethylformamide(DMF) solutions at mercury pool electrode yielded selectively the corresponding chlorine reduced products in moderately good yields.

The electrochemical reduction of α , β-unsaturated aldehydes and ketones has been extensively studied in various media(1-4). In contrast, the electrochemical studies of the corresponding unsaturated imines have received very little attention and, as such, few reports are available in the literature, wherein only the basic electrochemical results obtained at the microelectrode were discussed(5,6). To our knowledge, the electrochemistry of β-halo-α, β-unsaturated aldehydes and their derivatives are not known, despite the fact that they are useful synthons and their chemistry is well established(7). Recently, we have observed an interesting transformation in the electrochemical reduction of the parent aldehyde, viz., 4-chloro-3-formyl-2H(1)-benzopyran in ethanol-water mixtures(8), while electrolysis in DMF afforded no characterisable products.



In contrast, the controlled-potential electrolyses of the corresponding Schiff's bases 1a-f in DMF afforded a selective cathodic reduction of the carbon-chlorine bond.

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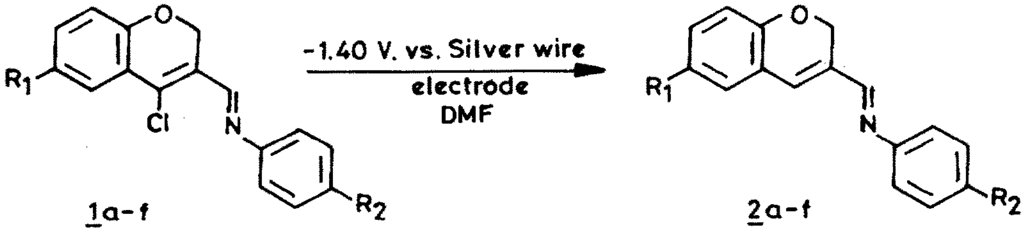
A series of chlorovinylimines, 1a-f were prepared according to the literature procedure earlier reported by us(9). A divided cell containing mercury pool as the working electrode and platinum foil as the anode was used for electrolysis(10). The electrolysis of 1a ($3.3 \times 10^{-2}$ M) was carried out at a constant potential of -1.40V vs. silver wire (reference electrode) in DMF solutions containing 0.1M tetrabutylammonium perchlorate ($NBu_4ClO_4$) as the supporting electrolyte. After the electrolysis (disappearance of the starting material vide tlc) the solvent was removed from the catholyte solution under reduced pressure and the residue repeatedly extracted with ether. Evaporation of the ether solution after workup gave a reddish brown solid. On triturating the crude product with a small quantity of methanol (2-3ml), a yellow solid was obtained which on recrystallization in hexane yielded pale yellow crystals (m.p. 86-88°C). The isolated electrolysis product was found to be identical with that of 3-(N-aryliminomethyl)-benzopyran, 2a (prepared chemically) in all respects.



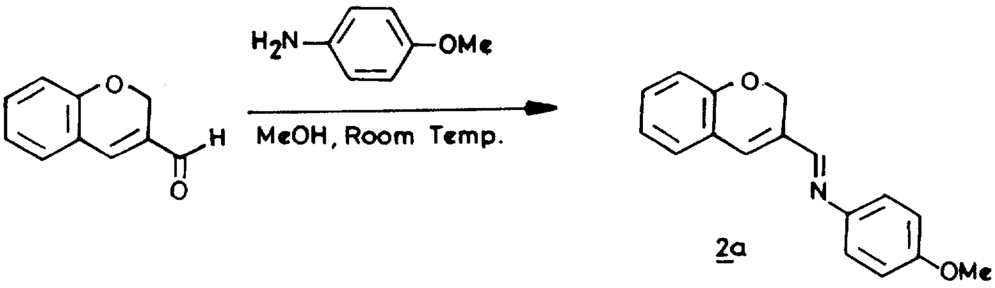
The macro-electrolysis was also extended to other chloroimines, 1b-f and the data pertaining to the electrolysis products are presented in Table.

**Table** : Physical constants and percentage yields of the electrolysis products, 2a-f:

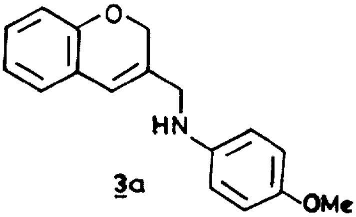
| Compound | $R_1$ | $R_2$ | m.p. (°C) | Percentage yield (isolated) |
|---|---|---|---|---|
| 2a | H | $OCH_3$ | 86-88 | 70 |
| 2b | H | $CH_3$ | 118-20 | 64 |
| 2c | H | H | 59-60 | 60 |
| 2d | $CH_3$ | $OCH_3$ | 90-92 | 66 |
| 2e | $CH_3$ | $CH_3$ | 101-2 | 62 |
| 2f | $CH_3$ | H | 88-9 | 60 |

The HPLC analysis of the crude product obtained in the electrolysis of 1a indicates the presence of 2a in major amounts (79%) together with 3a (15%) and another product (to be identified) in trace amounts (6%). The retention times of the electrolysis products 2a and 3a were found to be in close agreement with that of the authentic samples prepared independently(11).

The product 3a could not be isolated from the crude electrolyzed mixture due to its instability.

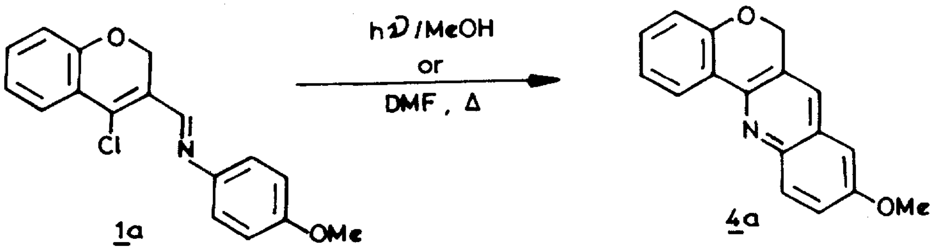


2a



3a

It may be mentioned here that both thermolysis (12) and photolysis (9) of these chlorovinylimines 1a afforded condensed (4,3-b) benzopyranoquinolines, 4a whereas, the electrochemical reduction yielded a selective reduction of the carbon-chlorine bond leading to the corresponding 3-(N-aryliminomethyl)-2H(1)-benzopyrans, 2a-f in moderately good yields.



1a

4a

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10. Basic electrochemical results will be published elsewhere.
11. The compound 3a was prepared by the sodium borohydride reduction of 2a in the solvent mixture containing methanol and tetrahydrofuran in the ratio 5:1.
12. Unpublished result.

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