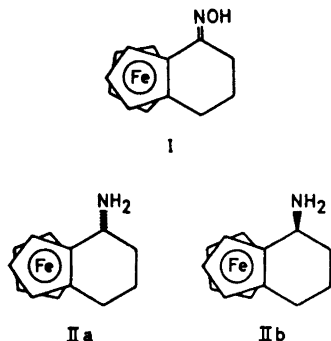


## Short Communications

On the Electrochemical Reduction of 1,2-( $\alpha$ -Ketotetramethylene)-ferrocene OximeSTIG ALLENMARK<sup>a</sup> and  
BERTIL HELGÉE<sup>b</sup><sup>a</sup> Department of Organic Chemistry,  
University of Uppsala, P.O. Box 531,  
S-751 21 Uppsala, Sweden. <sup>b</sup> Department of  
Organic Chemistry, University of Lund,  
P.O. Box 740, S-220 07 Lund, Sweden

The stereoselective sodium-ethanol reduction of 1,2-( $\alpha$ -ketotetramethylene)-ferrocene oxime (I) to *endo*-1,2-( $\alpha$ -aminotetramethylene)-ferrocene (IIa) was recently reported.<sup>1</sup> The results obtained by Fry,<sup>2,3</sup> who found dissolving metal reduction and electrochemical reduction of bicyclic oximes to occur with quite opposite stereochemistry, thus prompted us to apply the latter method on I.



The results from the reductions of I are summarized in Table 1. Completely  $\alpha$ -deuteriated II was obtained, as shown by PMR, when the electrolysis was carried out in ethanol-*d*<sub>1</sub>/D<sub>2</sub>O.

Table 1. Stereochemical results and yields in reductions of I.

Reducing agent	Total yield <sup>a</sup> (%) of II	Relative amounts	
		% IIa	% IIb
Na-EtOH	40-55	>97	<3
Hg-cathode	65-76	~80	~20

<sup>a</sup> The possible recovery of starting material (I) has not been taken into account here.

The better yield obtained on electrolysis is clearly accompanied by a decrease in stereoselectivity. With both methods, however, the *endo*-isomer IIa is the predominant product, a result which is in marked contrast to those reported earlier.<sup>3</sup>

There are good reasons for believing that the stereochemistry of the dissolving metal reduction is kinetically controlled by protonation of the initially formed anion-radical by the solvent from the (least hindered) *exo*-side, thus yielding almost exclusively IIa. No *exo-endo*-equilibration occurs under the conditions used, which excludes thermodynamic control. The electrochemical result is more difficult to interpret, especially since the detailed mechanism of oxime electrolysis<sup>4</sup> is not yet known. The observed stereochemistry is, however, similar to that found for the bicyclic system in so far as the electrode attack and protonation steps involved<sup>2</sup> occur preferentially from the least hindered side in both cases.

The main difference, it may be noted, thus lies in the sodium-ethanol reduction of I and of the bicyclic oximes, respectively. The reason why the thermodynamically more stable amines are formed from camphor oxime and norcamphor oxime is still a matter of question.

*Experimental.* The preparation of I and its reduction with sodium-ethanol has been described earlier.<sup>1</sup> The electrolyses were carried out at a mercury pool cathode in a cell of conventional design equipped with a ceramic cup for separation of anode and cathode compartments. The anolyte was 0.1 M tetrabutylammonium tetrafluoroborate in ethanol/water solution (9/1 by volume). The catholyte contained 2 mmol (538 mg) of the oxime I in 50 ml of the same solvent-supporting electrolyte system as the anolyte. The electrolyses were run at a constant current of 0.25 A until 6 F/mol of substrate had passed. On work-up the catholyte was made weakly acidic with dilute hydrochloric acid and the solvent evaporated. The residue was diluted with a sodium hydrogen carbonate solution and repeatedly extracted with ether. Drying and evaporation of the ether solution yielded the crude amine II. This could be purified by extraction of the amines from the ether solution with 0.1 M hydrochloric acid, precipitation with dilute alkali and isolation of the product by extraction with ether, drying and evaporation.

The *endo/exo*-ratios (IIa/IIb) were determined either directly from the PMR-spectrum of the product II by integration of the peak-areas corresponding to the  $\alpha$ -methine proton and cyclopentadienyl ring proton resonance signals, or by means of a chromatographic separation of IIa and IIb.<sup>5</sup>

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## 5-Amino-2-formylimidazo [1,2-a]pyridine

OLOF CEDER, KENNETH ROSÉN and  
JOHN F. WITTE

*Department of Organic Chemistry, University of Göteborg and Chalmers Institute of Technology, Fack S-402 20 Göteborg 5, Sweden*

In an attempt to synthesize 1,4-diazacycl[3.2.2]azine, 7, in a "one-step" reaction (cf. Chart 1), 2,6-diaminopyridine, 1, was condensed with bromomalondialdehyde, 2 (X = Br). A yellow solid with the composition  $C_8H_7N_3O$  was obtained in 17% yield. Its IR spectrum shows aldehydic C-H absorption at 3730 and 2820  $cm^{-1}$

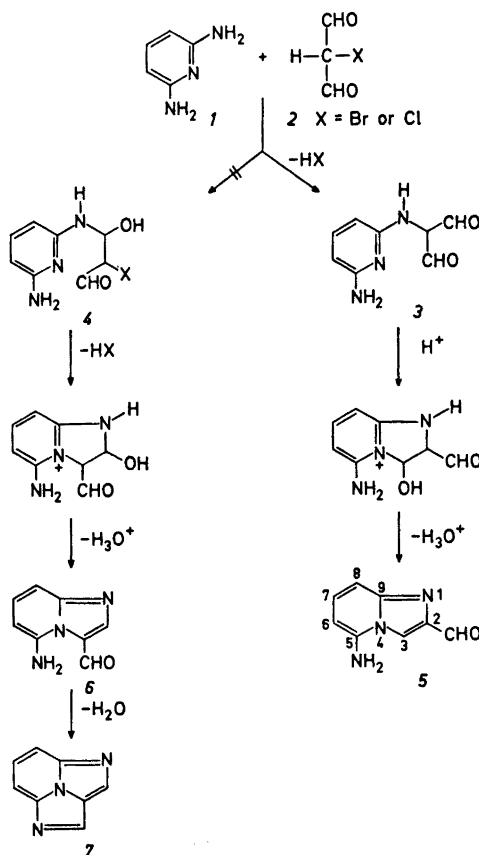


Chart 1.