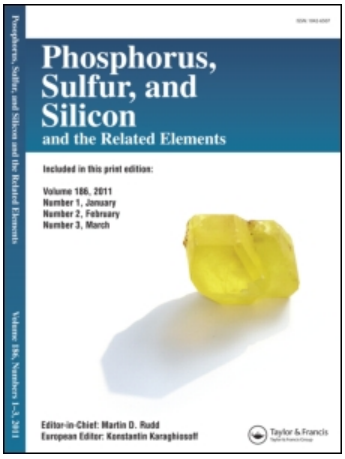

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Selective Electroreduction of Substituted 1,3-Thiazinic Compounds

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SELECTIVE ELECTROREDUCTION OF SUBSTITUTED 1,3-THIAZINIC COMPOUNDS

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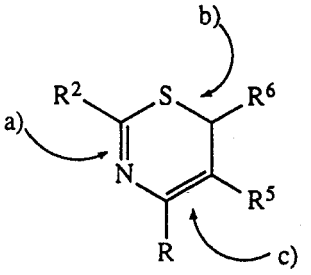
Controlled potential electrolysis of 1,3-thiazinic derivatives are investigated in protic medium. Generally selective dihydrogenation is observed. However ring opening or ring contraction reduction can also take place.

Many applications of dihydro and tetrahydro-1,3-thiazinic derivatives are mentioned in the literature. Flexible methods for the preparation of unsaturated 6H-1,3-thiazines A, 4H-1,3-thiazines B and 6H-1,3-thiazine-6-ones C are well known[1].

Selective electroreduction of these compounds is performed at a mercury cathode in aqueous alcoholic medium.

In the A series, clean and chemioselective electroreduction of the heterocycle skeleton is observed, depending on the substitution[2].



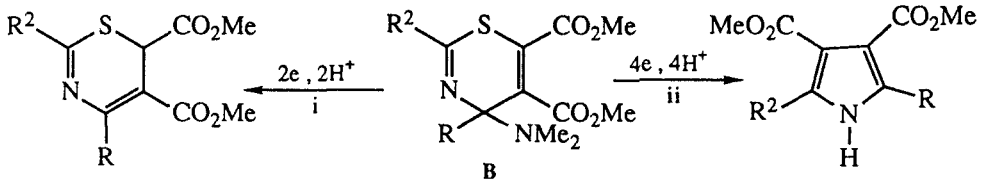
A

a) 1 electron reduction leading to duplication at the C^2 position and 2 electron reduction giving 2,3-dihydro derivatives occur for 5-monoactivated compounds.

b) 2 electron reduction with hydrogenolysis of the C^6-S bond takes place for 4-monoactivated derivatives.

c) 2 electron reduction of the C^4-C^5 double bond (dihydro) followed by 2 electron reduction at the C^2-N(tetrahydro) is obtained for 4,5-diactivated 1,3-thiazines. On the opposite, chemical reduction can begin at the C^2-N showing complementarity between chemical and electrochemical methods.

In the **B** series, the orientation of the electroreduction appears to be dramatically pH dependent[3].

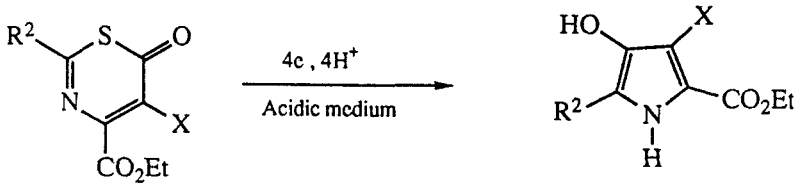


i : acetic or ammoniacal buffer ; ii : 0.5 M sulfuric solution

* In acetic or ammoniacal buffer, polysubstituted 6H-1,3-thiazines are preferentially obtained. These results are extented as a methodological way for an easy access to 6-activated 6H-1,3-thiazines[4].

* In 0.5 M sulfuric medium, unexpected formation of 1H-pyrroles resulting from ring contraction with sulfur extrusion is observed. Chemical, electrochemical and sonochemical access to these substituted 1H-pyrrole from 4H-1,3-thiazines are compared[5].

Development of preliminary results[6] on the electroreduction of 6H-1,3-thiazine-6-ones shows the possibility to isolate substituted 3-hydroxy-pyrroles in acidic medium.



R^2 = Ph, $PhCH_2S$

X = H, Ph, CO_2R', OR'

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