

**CONVERSIONS OF NITROGEN-CONTAINING
HETEROCYCLES INDUCED BY ELECTRON**

TRANSFER

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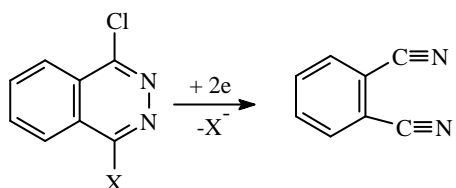
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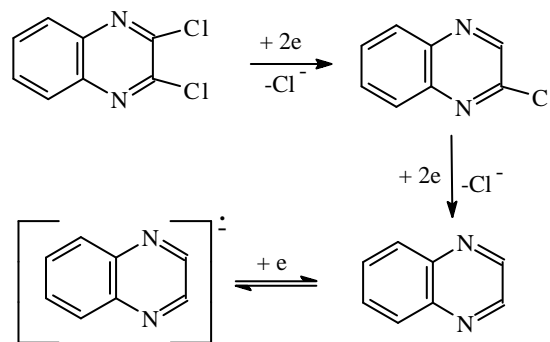
The heterocyclic compounds are very important in modern chemistry. The electrochemical reactions of nitrogen-containing heterocycles are of interest both from the point of view of the electrosynthesis of new nitrogenorganic compounds, and from the point of view of an estimation of a specific role of heteroatoms in the processes of electron transfer in chemical and biochemical systems. We have studied the electrochemical reduction of some of heterocyclic compounds and we have found new transformation of heterocycles. Reduction of 1,4-dichlorophthalazine results in elimination of two anions, the cleavage of the N-N-bond, the opening of the ring, and the formation of phthalonitrile. The overall process includes the transfer of two electrons, the cleavage of three σ -bonds, and the formation of two new π -bonds. It is the first example, when the electron transfer induces such deep reorganization of a particle. The reduction of alkylthio-, arylthioalkoxy- and phenoxy-phthalazines proceeds on analogous scheme with pyridazine ring opening, elimination of two anions, and formation of phthalonitrile. In this case the simultaneous heterogeneous and homogeneous (by phthalonitrile anion radical) reduction of this compound takes place at the first wave potentials. The reduction of oxy- and aminophthalazines proceeds differently, without the formation of phthalonitrile. We have introduced electrochemical criterion of realization of this or that reduction process of 1-chloro-4-X-phthalazines. The compounds with half-wave potentials $-1.42 \div -173$ V (vs. SCE). are reduced with elimination of X-group, and the compounds with more negative potentials are reduced without elimination of X-group. For the symmetric 1,4-bisalkoxy-, bisphenoxy-, bisalkylthio- and bisphenylthiophthalazines in none of the cases the heterocyclic ring opening was found. Initial anion radicals are detected for all compounds; for some compounds at lower temperatures, for others - at room temperature.



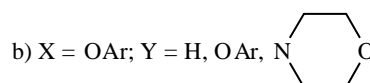
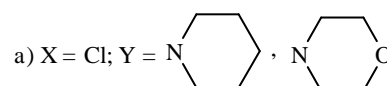
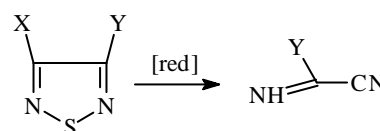
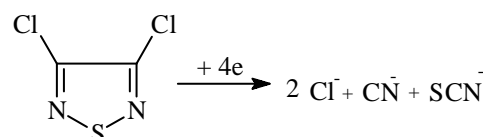
X = H, Cl, OAlk, OAr, SAlk, SAr

The elimination of chloride-ion from position 6 is observed for 1,4,6-trichlorophthalazine which is also ended by opening of pyridazine cycle.

In the case of 1,4-dichlorohinoxalin the reduction is stopped when anion radical of hinoxalin was formed.



The reduction of 3,4-dichloro-1,2,5-thiadiazole leads to disintegration of heterocycle and formation of inorganic ions. The other of thiadiazoles reduce to iminonitriles.



Obtained results show that the electron transfer on the molecule of phthalazines and thiadiazoles induced the breakup of N-N linkage, when compound have two groups capable of anionic elimination.

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