Mechanistic and Synthetic Aspects of N-arylazoles formation in undivided electrolysis of the mixture azole / arene in MeCN

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The electrolysis of the mixture azole / azole salt / arene in an undivided cell opens new possibilities of the C–N bond construction. According to the data of (1) the mechanism of transformation of 3-nitrotriazole and 1,4-dimethoxybenzene (DMB) or benzene into corresponding N-arylazoles **1** may be depicted with the Scheme 1 which is consistent with the results of more late research (2). According to (1) the presence of the “ready” anionic nucleophiles (azole salt in the initial reaction mixture) is essential in the starting of the electrolysis since afterwards the reasonable concentration of nucleophiles is maintained by the cathodic deprotonation of the azoles.

Upon further developing these works we obtained new data concerning electrosynthesis of N-arylazoles in amperostatic undivided electrolysis (Pt, MeCN, Bu_4NClO_4) from 1,4-, 1,3- and 1,2-DMB and the azoles (pyrazoles, 1,2,4-triazoles and tetrazole), and some results turned out to be unexpected. It was first established that the electrolysis of mixture azole / 1,4-DMB results, alongside with *ortho*-substituted products **1**, in the hydrolytically labile products of *ipso*-bisaddition **2**. It was found that N-arylazoles are formed in the mixture lacking azole salt and also upon addition to such mixture of base (collidine - Col) or, notably, even of the acid (AcOH). Moreover, the N-arylazoles were formed also in the electrolysis of mixture azole / 1,4-DMB in anodic compartment of the divided cell. These results pointed to the imperfection of previously proposed mechanism of the process. We demonstrated that the role of nucleophiles is played in main part not by the azolate anions but, instead, by the hydrogen bond based complexes of azoles with each other or with Col (AzH•B, B = AzH, Col). And the cathodic process is in turn contributed, essentially, not by the generation of azolate anions (that is principally possible) but by the deprotonation of onium compounds (BH^+) resulting from interaction of azoles or Col with protons. Curiously enough, the complexes AzH•Col are sufficiently polar and, for the most acidic azoles, are, in fact, ion pairs.

In general, the body of experimental data (3) allows of description of process mechanism by the Scheme 2. We believe that the benzene ring of radical cation **4** undergoes alternative *ortho*- or *ipso*-attack of nucleophile (AzH•B or Az^-) resulting in radicals **5** and **6** capable of oxidation to cations **7** and **8**, correspondingly. The deprotonation of **7** leads to the *ortho*-substituted product whereas the *ipso*-interaction of **8** with nucleophile leads to the product of *ipso*-bisaddition **2**. More delicate details of the process are connected with rearrangement of arenonic cation **8** to the corresponding cation **7** the possibility of which was independently confirmed by the chemical experiments. The mechanism of rearrangement is discussed which is most likely different for high basic (2,5-dimethylpyrazole) and low basic (tetrazole) azoles and proceeds, probably, *via* intermediates **9** and **10**, respectively. Also discussed is the possibility of transformation **2** + **4** → **5** + **8** and acid catalysed transformation **2** → **8**. The effect of DMB structure (1,4-, 1,3- and 1,2- isomers) on the process mechanism is concidered.

References.

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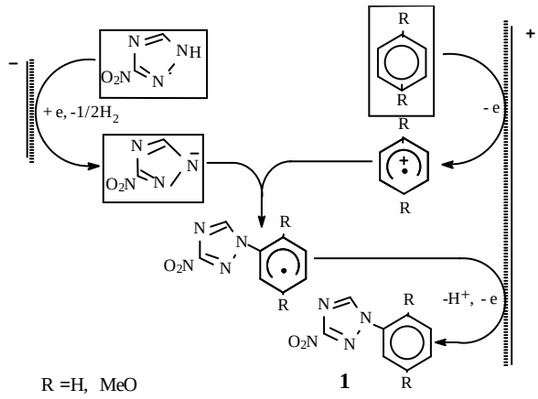
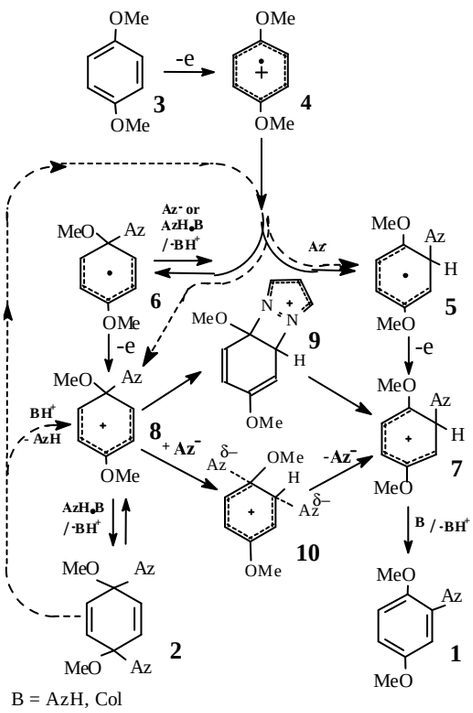


Scheme 1.



Scheme 2.