HETEROCYCLES, Vol. 57, No. 2, 2002, pp. 219-222, Received, 1st November, 2001

ELECTROCHEMICAL REACTIONS OF DIHYDROAZAAZULANONES POSSESSING A SPIROCYCLIC MOIETY: RING CLEAVAGES OF THE SPIRO-RINGS, HYDROGEN MIGRATIONS AND FORMATIONS OF AZAAZULANONES

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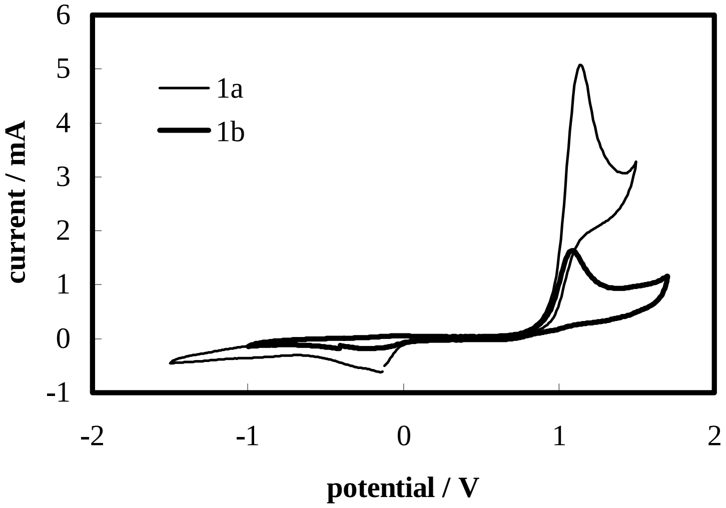
Abstract – Electrochemical oxidations of dihydroazaazulanones possessing a spirocyclic moiety afforded two types of dihydroazaazulanones and one type of azaazulanones. The reaction is considered to proceed *via* a ring cleavage of the spiro-three membered ring followed by a hydrogen migration.

As a member of nonbenzenoid aromatic compounds, the chemistry of bicyclo[5.3]deca-3,4,6,8-tetraen-2-ones (azulanones) has been researched extensively.[1] The aza-analogs of the azulanones, cyclohepta[*b*]pyrrol-2(1*H*)-one (azaazulanone) derivatives and its dihydro isomer, 1,2,3,3*a*-tetrahydrocyclohepta[*b*]pyrrol-2-one (dihydroazaazulanone) derivatives have attracted attention of chemists not only from view points of their physical and chemical properties but also from their pharmacologocal activities.[2]

The dihydroazaazulanone skeleton contains a cycloheptatriene and a carbonyl group connected by a sp^2 hybridized nitrogen atom constructing a 10π-electrons conjugated system containing two hetero atoms. The authors have researched on the chemistry of these compounds,[3] and reported on the synthesis of dihydroazaazulanone derivatives (**1**) possessing a norcaradiene system as a spirocyclic moiety by cycloaddition reactions of iminotropones with 8-oxoheptafulvene.[4] As a series of our researches on the reactivities of dihydroazaazulanone derivatives, we studied the electrochemistry of the title compounds. Here the results are reported.

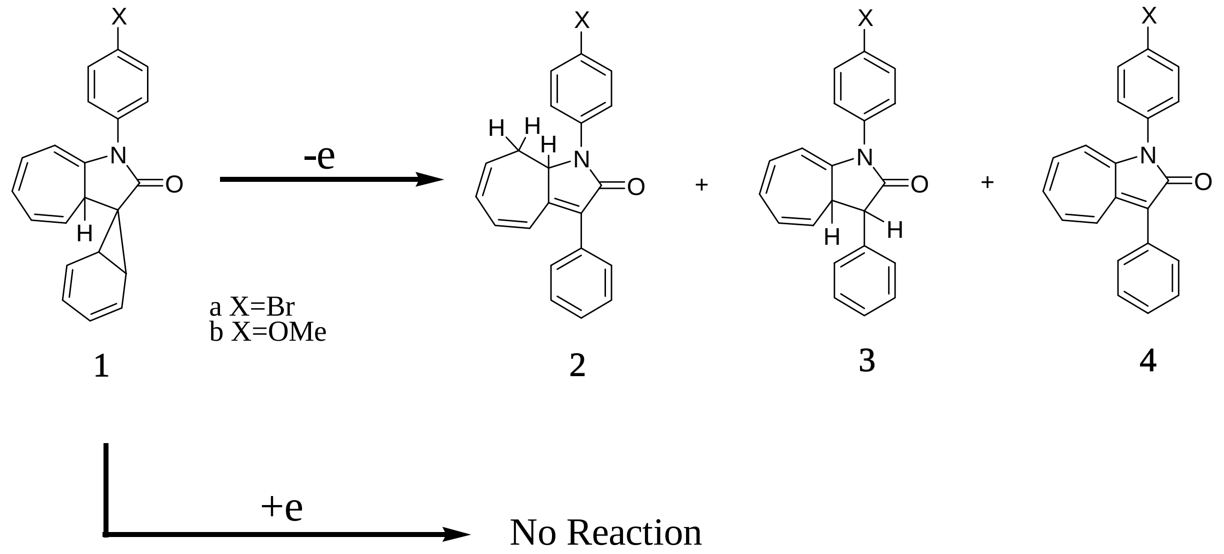
The following Figure presents cyclic voltammograms of the dihydroazaazulanones (**1a** and **1b**) possessing a spirocyclic moiety.[5] Both of them show oxidation peaks at *ca*. +1.1 V vs. Ag/AgCl.



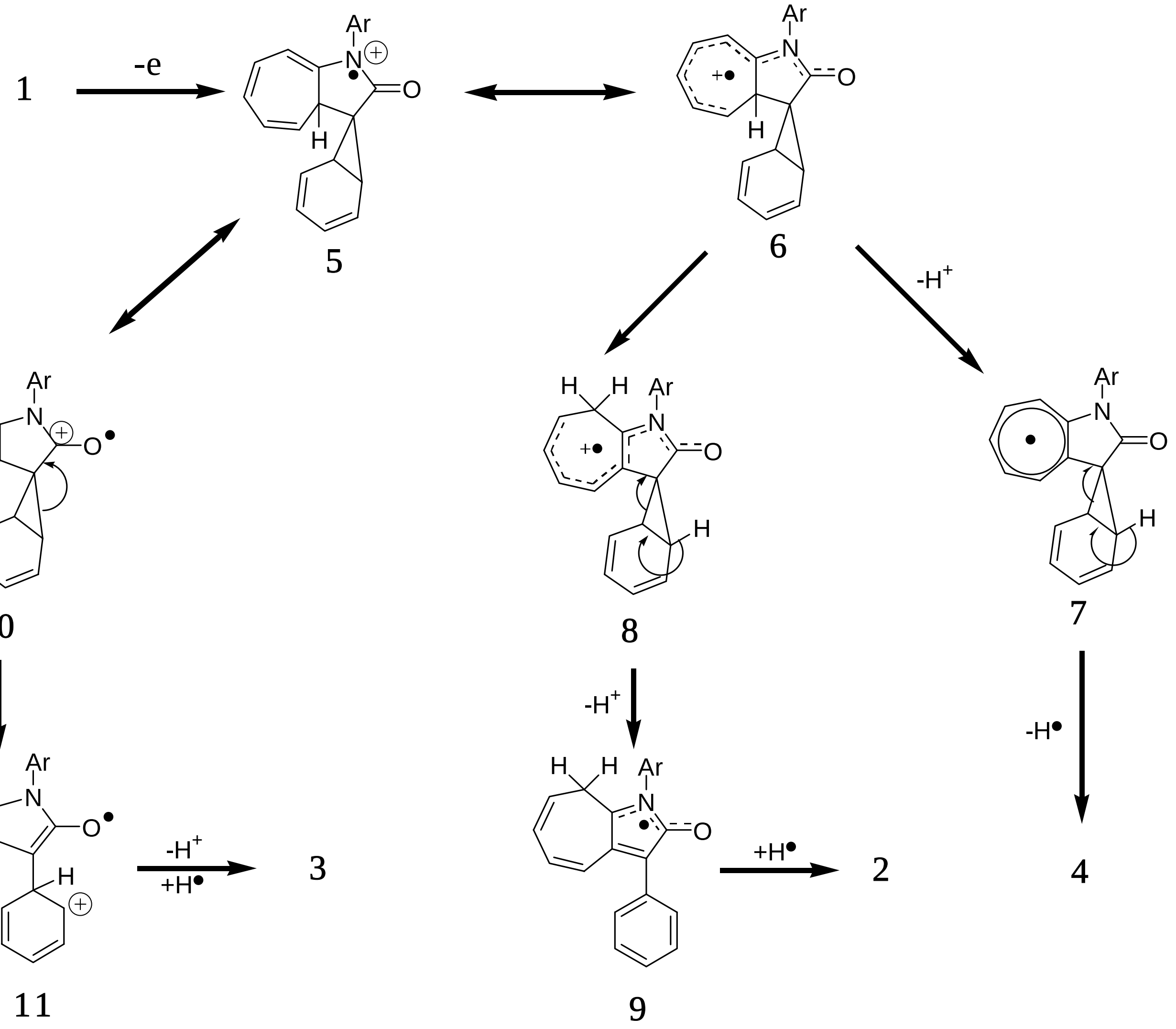
Electrochemical reductions of **1a** or **1b** at –1.4 V vs. Ag/AgCl in methylene chloride failed to give any isolable products and the starting materials were mostly recovered.[6] On the other hand, electrochemical oxidation of **1a** at +1.3 V vs. Ag/AgCl in methylene chloride afforded three kinds of products (**2a**, **3a**, and **4a**) in 47, 25, and 17 % yields, respectively.

The analogous result was obtained in the reaction with **1b** to form **2b**, **3b**, and **4b** in the yields of 42, 42, and 15 %, respectively.

No mutual conversions between **2**, **3**, and **4** were observed under the reaction conditions.



The structures of azaazulanone derivatives (**4**) were determined on the basis of the coincidences of their spectral properties with those of the authentic samples.[7] The structures of **2** and **3** were established on the basis of their spectral properties,[8] and further supported by their almost quantitative formation of **4** by oxidation reactions with DDQ.



The reaction mechanism is considered to be as follows. An electrochemical one-electron oxidation at the lone pair electrons of the nitrogen atom of 1 generates a cationic intermediate (5). An elimination of a proton from the canonical formula (6) of 5 forms a radical intermediate (7). A successive elimination of a hydrogen radical concerted with a ring opening process at the spiro-three membered ring in 7 can form the final product, azaazulanone derivative (4).

On the other hand, a 1,3-hydrogen migration process in a cationic intermediate (6) generates an another type of a cationic intermediate (8), which then affords 2 *via* a ring opening process of the spiro-three membered ring accompanied by an elimination of a proton. A molecular orbital calculation with a PM 3 method showed the heat of formation of 8 (1314 kJ) to be lower than that of 6 (1494 kJ) supporting the appropriateness of the molecular rearrangement of 6 to 8.

A ring opening process of the spiro-three membered ring in the canonical formula (10) of 5 forms an enole radical type intermediate (11), which can afford 3 through an elimination of a proton and abstraction of a hydrogen radical.

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4. Y. Saito, M. Tomita, H. Taniguchi, H. Okabayashi, and K. Saito, *Heterocycles*, 1995, **41**, 2181.
5. The cyclic voltammograms of **1a** and **1b** (0.5 mM) were performed with a platinum electrode in acetonitrile in the presence of 0.1 M TBAP (tetra-n-butylammonium perchlorate) with a scan rate $\boldsymbol{\nu}$ = 200 mV s^{-1}.
6. The electrochemical reactions were performed in dichloromethane or acetonitrile (200 mL) with dihydroazaazulanones (**1a** or **1b**, 0.5 mmol), TBAP (17.5 mmol) as a supporting electrolyte, a platinum gauze as a working electrode, and a platinum rod as a counter electrode in a divided-cell at 0 ℃ under a nitrogen atmosphere.
7. K. Ito, K. Saito, and K. Takahashi, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 812.
8. The NMR spectra of the selected products are as follows.
   2a:^{1}HNMR ($CDCl_3$) $\boldsymbol{\delta}$: 2.48 (m, 1 H), 2.82 (ddd, 1 H, *J* = 17.3, 8.0 and 3.0 Hz), 4.94 (dd, 1 H, *J* = 13.5 and 2.9 Hz), 6.10 (m, 3 H), 6.65 (d, 1 H, *J* = 11.3 Hz), 7.36-7.62 (m, 9 H). ^{13}CNMR ($CDCl_3$) $\boldsymbol{\delta}$: 29.7, 58.3, 117.7, 122.5, 123.5, 127.8, 128.0, 128.2, 128.4, 129.5, 129.8, 130.1, 130.4, 130.6, 131.9, 135.6, 149.7.
   3a:^{1}HNMR ($CDCl_3$) $\boldsymbol{\delta}$: 3.11 (m, 1 H), 4.01 (d, 1 H, *J* = 4.9 Hz), 5.38 (dd, 1 H, *J* = 8.9 and 3.5 Hz), 5.47 (dd, 1 H, *J* = 6.6 and 1.4 Hz), 6.25 (m, 2 H), 6.41 (dd, 1 H, *J* = 10.4 and 6.6 Hz), 7.20-7.60 (m, 9 H). ^{13}CNMR ($CDCl_3$) $\boldsymbol{\delta}$: 44.6, 54.6, 100.2, 122.2, 122.8, 125.9, 127.5, 127.6, 127.9, 128.4, 128.9, 129.1, 129.2, 132.4, 132.8, 138.2, 175.3.