ELECTROCHEMISTRY OF 1,3-DIAZADIHYDROAZULANONE: ELECTROCHEMICAL REDUCTION AND OXIDATION OF 1-TOSYL-3-ARYL-1,3-DIAZADIHYDROAZULANONE LEADING TO MIGRATION AND ELIMINATION OF THE TOSYL GROUP

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Abstract - Electrochemical oxidations of 1-tosyl-3-aryl-1,3-diazadihydro-azulanones gave 6-tosyl-3-aryl-1,3-diazadihydroazulanones *via* migrations of the tosyl group. On the other hand, electrochemical reductions of the 1-tosyl-azulanones afforded 3-aryl-1,3-diazadihydroazulanones through eliminations of the tosyl group.

The 1,3-diazadihydroazulanone system (**1**) is composed from two parts, *i.*e., a cycloheptatriene and a diazacyclopentanone parts. Considering the sp^2 hybridization of the two nitrogen atoms, this system can be regarded to have a 12 electrons cross conjugation system.[1] As a series of our research on the cycloaddition reactions of heterocumulenes, we have documented on the synthetic approach to this system[2] and have pointed out a good possibility of this system to be converted to organic electroconductors.[3] Recently, we reported on the electrochemistries of several heterocyclic compounds to proceed ring opening, ring contraction, or hydrogen migration reactions.[4] These facts prompted us to investigate the electrochemistry of **1**. Here the results are discussed.

A solution of 1-tosyl-3-(*p*-methylphenyl)-1,3-diazadihydroazulanone (**1a**) in anhydrous acetonitrile was electrochemically oxidized in the presence of tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte with a platinum gauze as an anode and a platinum wire as a cathode at 1.3 V vs. Ag/Ag$^+$ at 0 under a nitrogen stream. After evaporation of the solvent, the reaction mixture was chromatographed on silica gel using *n*-hexane ethyl acetate (7:3) as a developing solvent to give 6-tosyl-3-(*p*-methylphenyl)-1,3-diaza-dihydroazulanone (**2a**)[5] in 52 % yield *via* a migration of the tosyl group. The current efficiency was 27 %.

The product yield of this reaction was not effected so much by the substituent of the aryl group of **1**. Thus, 1-tosyl-3-(*p*-methoxyphenyl)- (**1b**), 1-tosyl-3-(*p*-chlorophenyl)- (**1c**), and 1-tosyl-3-(*p*-bromo-phenyl)-1,3-dizadihydroazulanone (**1d**) were electrochemically oxidized under analogous reaction conditions as above to give the corresponding products **2b**, **2c**, and **2d** in 56, 59, and 44 % yields, respectively. The current efficiencies were 40, 31, and 27 %, respectively.

The structure of **2a** was deduced mainly on the basis of ^{1}H NMR, MS and IR spectra and confirmed by the good resemblance of these to those of the analogues compound.[6] Mass spectrum indicated that the molecular ion peak of **2a** (M$^+$, 329) was consisted with the molecular weight of the starting material (**1a**). An absorption at 3420 cm^{-1} in IR spectrum showed a presence of an N-H bond. 1H NMR spectrum taught an existence of a chain of five continued carbon atoms of C_4-C_8, in which only C_6 is a saturated carbon atom connected to a tosyl group. Considering the chemical shifts of the corresponding protons of the analogous compounds,[6] the assignment of each proton was decided to be as shown in the Figure.

a: X=Me b: X=OMe
c: X=Cl   d: X=Br
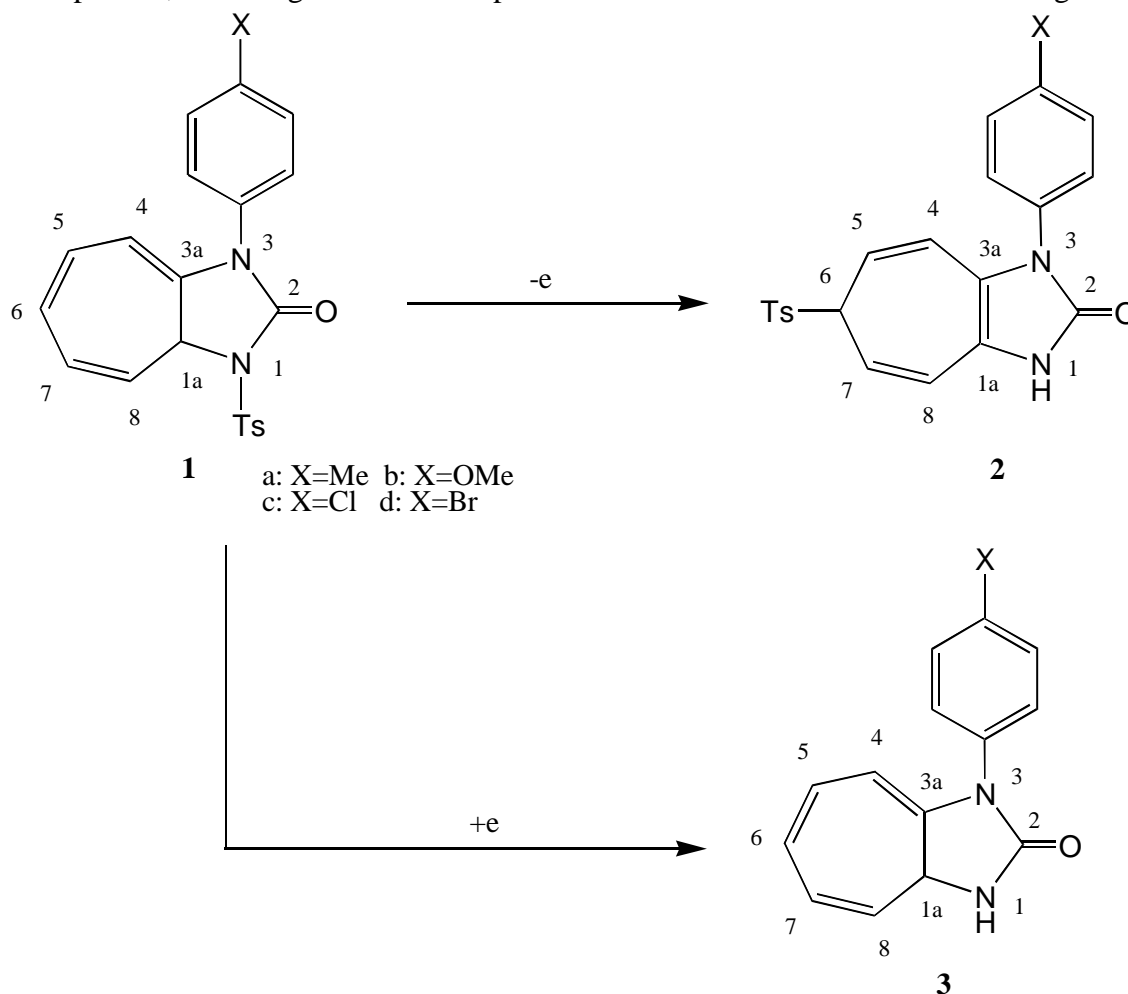
The electrochemical reductions of **1** resulted in eliminations of the tosyl group to afford 3-aryl-1,3-diazadihydroazulanone derivatives (**3**)[7]. The product yields were fairly influenced by the substituent on the aryl group. Thus, the electrochemical reduction of **1**, which has an electron donating substituents on the aryl group (**1a**, **1b**), did not proceed smoothly, and a large intractable resinous material was produced along with the purely isolated product (**3**), as shown bellow.

A solution of **1a** in anhydrous acetonitrile was electrochemically reduced in the presence of TBAP using a platinum wire as an anode and a platinum gauze as a cathode at –1.2 V vs. Ag/Ag$^+$ at 0   under a nitrogen stream. A usual treatment of the reaction mixture gave a low yield (10 %) of **3a**. The current efficiency was very low (4 %).

The reduction of **1b** gave **3b** in 7 % yield with the current efficiency 3 %. On the other hand , the reductions of **1** possessing an electron withdrawing substituent on the aryl group afforded the corresponding products in proper yields: thus **1c** and **1d** formed **3c** and **3d** in 51 and 25 % yields with the current efficiencies 41 and 14 %, respectively.

The structures of the products (**3**) were confirmed by a good coincidence of their spectral properties with those of the authentic samples.[2-4,8]

Table 1. Redox Potentials.

| X	Oxidation	Reduction
Me	1.24	-1.02
OMe	1.23	-0.85
Cl	1.19	-0.71
Br	1.21	-0.84

V vs. Ag/AgCl

On the other hand, some scattering is observed in the reduction potentials. This scattering and the large negative value of the reduction potential of **1a** (X=Me) show that the reduction potentials depend on the substituents on the aryl group. Thus, in the case of reduction, the coming electron is considered to be received in the diazadihydroazulanone skeleton.

The redox potentials of **1** measured with cyclic voltammetries are summarized in the Table 1.[9] No substituent effects are observed on the oxidation potentials suggesting that these potentials are attributable to the oxidation of the tosyl group. Thus in the case of electrochemical oxidation of **1**, the initial stage is considered to be an elimination of an electron on the tosyl group.
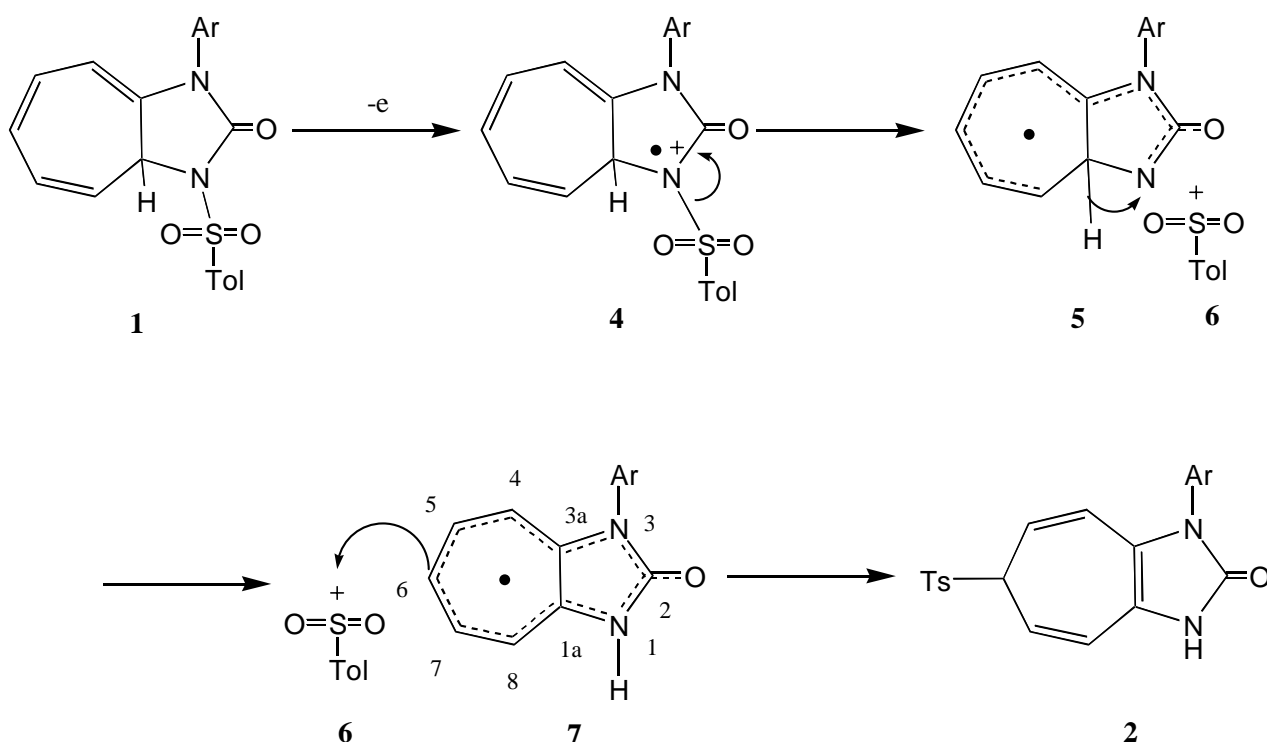
The reaction mechanism of the electrochemical oxidation is proposed as follows. One electron oxidation occur a removal of one electron from the nitrogen atom at 1-position on **1** to form a cation radical intermediate (**4**). An N-S bond fission in **4** generates a radical intermediate (**5**) and a tosyl cation (**6**). A hydrogen migration in **5** forms a full conjugated radical intermediate (**7**). The neucleophilic attack at 6-positon on the radical intermediate **7** to tosyl cation **6** followed by an electron transfer from either the solvent or the supporting electrolyte can form the final product (**2**).
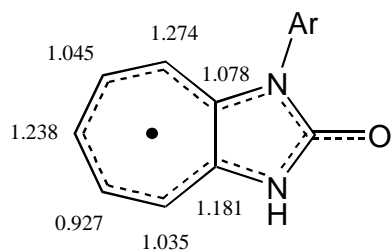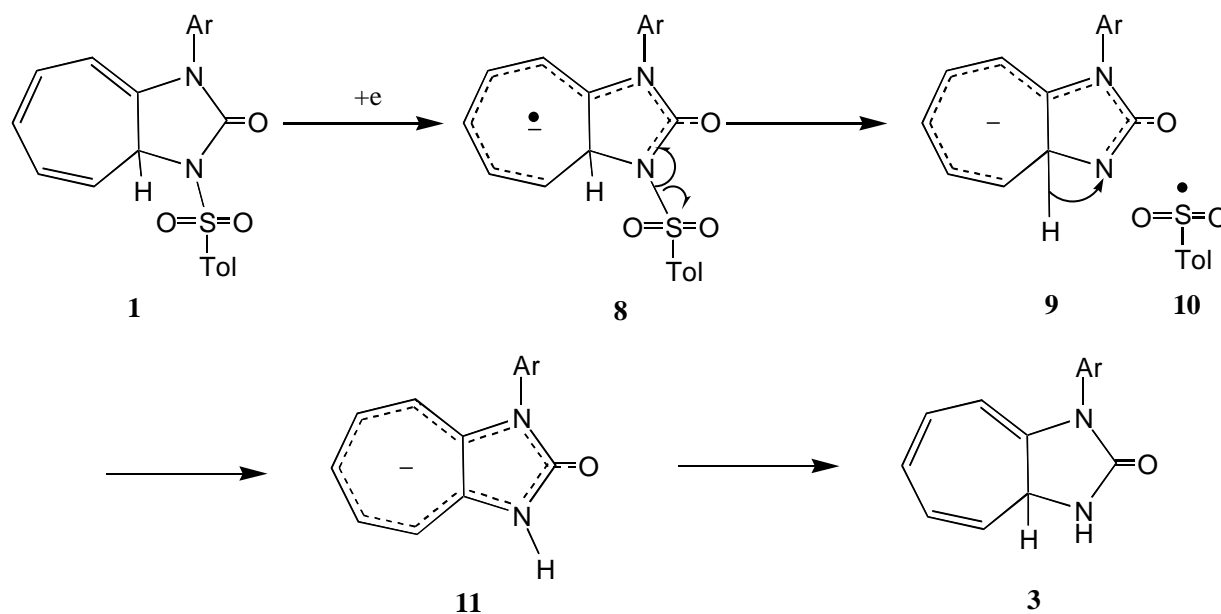

Free Valencies of **7**
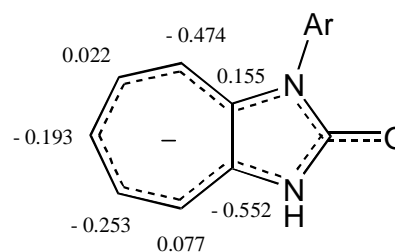
Electron Densities of **11**
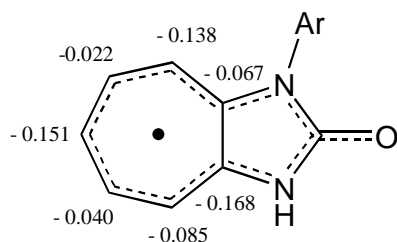
Electron Densities of **7**

The preferential recombination of the tosyl group on 6-position of **7** can be explained by the free valencies calculated by PM3 method, which show the second maximum value at the 6-position and/or by the electron densities which show the maximum value at the 6-position. [10]

1   8   9   10

11   3

The electrochemical reduction is considered to be proceed as follows. One electron reduction forms an anion radical intermediate (**8**), which then removes a tosyl radical (**10**) to form an anion intermediate (**9**). A hydrogen migration in **9** forms a full conjugated anion intermediate (**11**), which abstracts a hydrogen from the solvent to form the final product (**3**). The maximum electron density of **11** at 1a-position can explain the preferential hydrogen abstraction of **11** at this position.[11]

In summary, we found that the 1,3-diazadihydroazulanone derivatives (**1**) afforded the tosyl migration product (**2**) under electrooxidation conditions and the tosyl elimination product (**3**) under electro-reduction conditions. Further studies on electrochemistries of the azulanone derivatives are currently in progress and will be reported in due course.

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5. The physical properties of **2a-d** are as follows.

2a: HRMS m/z 392.1185. Calcd for $C_{22}H_{20}N_2O_3S$: 392.1178. MS m/z (rel intensity). 392 (16, M^+), 278 (9), 262 (6), 237 (26), 236 (100), 235 (73). ^{1}H-NMR (CDCl$_3$) ppm. 2.26 (1H, dd, H_6, J = 6.0 and 6.0 Hz), 2.38 (3H, s), 2.42 (3H, s), 4.30 (1H, bs, NH), 5.20 (1H, dd, H_5, J = 6.0 and 9.7 Hz), 5.47 (1H, dd, H_7, J = 6.0 and 10.2 Hz), 6.18 (1H, d, H_4, J = 9.7 Hz), 7.10 (1H, d, H_8, J = 10.2 Hz), 7.20 (4H, m), 7.36 (2H, d, J = 7.5 Hz), 8.01 (2H, d, J = 7.5 Hz). IR (KBr): 3420, 1718, 1375, 1172 cm^{-1}.

2b: HRMS m/z 408.1161. Calcd for $C_{22}H_{20}N_2O_4S$: 408.1153. MS m/z (rel intensity). 408 (14, M^+), 278 (17), 253 (23), 252 (100), 251 (33). ^{1}H-NMR (CDCl$_3$) ppm. 2.27 (1H, dd, H_6, J = 6.2 and 6.2 Hz), 2.45 (3H, s), 3.84 (3H, s), 4.30 (1H, bs, NH), 5.22 (1H, dd, H_7, J = 6.2 and 10.2 Hz), 5.50 (1H, dd, H_5, J = 6.2 and 9.7 Hz), 6.15 (1H, d, H_4, J = 9.7 Hz), 7.13 (1H, d, H_8, J = 10.2 Hz), 7.23 (4H, m), 7.37 (2H, d, J = 7.5 Hz), 8.04 (2H, d, J = 7.5 Hz). IR (KBr): 3423, 1721, 1379, 1178 cm^{-1}.

2c: HRMS m/z 412.0653. Calcd for $C_{21}H_{17}N_2O_3SCl$: 412.0647. MS m/z (rel intensity). 412 (14, M^+), 259 (90), 257 (100), 215 (72). ^{1}H-NMR (CDCl$_3$) ppm. 2.30 (1H, dd, H_6, J = 6.1 and 6.1 Hz), 2.44 (3H, s), 4.40 (1H, bs, NH), 5.24 (1H, dd, H_7, J = 6.1 and 9.9 Hz), 5.47 (1H, dd, H_5, J = 1.1 and 9.7 Hz), 6.18 (1H, d, H_4, J = 9.7 Hz), 7.12 (1H, d, H_8, J = 9.9 Hz), 7.30 (4H, m), 7.58 (2H, d, 7.5 Hz), 7.99 (2H, d, J = 7.5 Hz). IR (KBr): 3425, 1721, 1374, 1173 cm^{-1}.

2d: HRMS m/z 458.0096. Calcd for $C_{21}H_{17}N_2O_3SBr$: 458.0120. MS m/z (rel intensity). 458 (7, M^+), 303 (95), 301 (100), 259 (61). ^{1}H-NMR (CDCl$_3$) ppm. 2.30 (1H, dd, H_6, J = 6.3 and 6.3 Hz), 2.46 (3H, s), 4.32 (1H, bs, NH), 5.27 (1H, dd, H_7, J = 6.3 and 10.5 Hz), 5.54 (1H, dd, H_5, J = 1.3 and 10.0

Hz), 6.16 (1H, d, H$_4$, J = 10.0 Hz), 7.13 (1H, d, H$_8$, J = 10.5 Hz), 7.24 (4H, m), 7.58 (2H, d, J = 7.5 Hz), 8.02 (2H, d, J = 7.5 Hz). IR (KBr): 3422, 1719, 1375, 1170 cm^{-1}.

6. The chemical shifts of H$_a$ and H$_b$ of the following compound are observed to be 6.12 ppm.

   T. Ido, A Thesis for a Masterate, Nagoya Inst. Tech., **1998**.
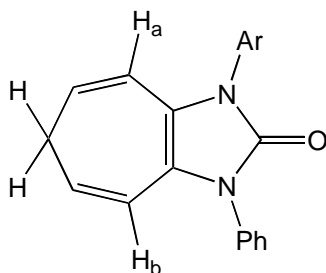
7. The ^{1}H NMR spectral properties of **3a-d** are as follows.

   3a: ^{1}H-NMR (CDCl$_3$)   ppm. 2.38 (3H, s), 4.20 (1H, bs), 5.16 (1H, dd, J = 9.6 and 3.0 Hz), 5.43 (1H, d, J = 6.9 Hz), 6.11 (1H, dd, J = 6.0 and 9.6 Hz), 6.23 (1H, dd, J = 11.1 and 6.0 Hz), 6.43 (1H, dd, J = 6.9 and 11.1 Hz), 7.25 (4H,m).

   3b: ^{1}H-NMR (CDCl$_3$)   ppm. 3.83 (3H, s), 4.20 (1H, bs), 5.16 (1H, dd, J = 9.6 and 3.0 Hz), 5.39 (1H, d, J = 7.0 Hz), 6.12 (1H, dd, J = 6.0 and 9.6 Hz), 6.24 (1H, dd, J = 11.3 and 6.0 Hz), 6.44 (1H, dd, J = 7.0 and 11.3 Hz), 6.98 (2H, d, J = 8.8 Hz), 7.26 (2H, d, J = 8.8 Hz).

   3c: ^{1}H-NMR (CDCl$_3$)   ppm. 4.18 (1H, bs), 5.17 (H, dd, J = 9.9 and 3.0 Hz), 5.47 (1H, d, J = 6.6 Hz), 6.14 (1H, dd, J = 6.3 and 9.9 Hz), 6.27 (1H, dd, J = 11.3 and 6.3 Hz), 6.45 (1H, dd, J = 6.6 and 11.3 Hz), 7.32 (2H, d, J = 8.5Hz), 7.43 (2H, d, J = 8.5Hz).

   3d: ^{1}H-NMR (CDCl$_3$)   ppm. 4.19 (1H, bs), 5.16 (1H, dd, J = 9.9 and 3.3 Hz), 5.59 (1H, d, J = 6.6 Hz), 6.14 (1H, dd, J = 6.3 and 9.9 Hz), 6.27 (1H, dd, J = 11.0 and 6.3 Hz), 6.45 (1H, dd, J = 6.6 and 11.0 Hz), 7.26 (2H, d, J = 8.5 Hz), 7.58 (2H, d, J = 8.5 Hz).

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9. The authors are indebted to Prof. Yoshiro Yamashita of the Institute for Molecular Science for his measurements of cyclic voltammetries.

10. The maximum value of the free valencies appears at 4-position. However the attack of the tosyl1 group at the 4-position of **11** seems to be avoided because of the steric hindrance caused by the adjacent aryl group.

11. A mechanism which affords **3** directly from **9**, seems to be still possible. The researches on the detailed reaction mechanism are now in progress.