ELECTROCHEMICAL REDUCTION REACTIONS OF 1,3-DIAZADIHYDROAZULANONE DERIVATIVES: 1,3- AND 1,5-HYDROGEN MIGRATION REACTIONS IN ELECTROCHEMICAL REDUCTIONS

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Abstract——Electrochemical reduction potentials of 1,3-diphenyl-1,3-diazadihydroazulanone derivatives were constructed from two stage reductions, each of which was influenced by the substituent on the phenyl group at 3-position. Electrochemical reductions of the diazadihydroazulanone derivatives afforded 1,3- and 1,5-hydrogen migration products, which isomerized each other under the reaction conditions. The reaction is considered to proceed *via* 1,3- or 1,5-hydrogen migrations through a radical anion intermediate generated by the reductions.

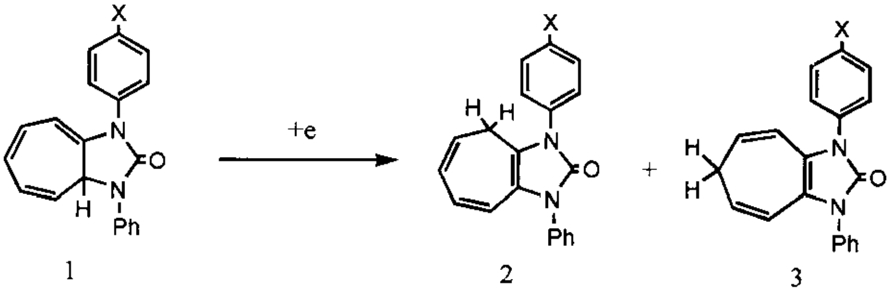
The π-conjugation network of the 1,3-diazadihydroazulanone system (1) contains two nitrogen atoms, one carbonyl group, and a triene moiety. Considering the sp^2 hybridization of the two nitrogen atoms, this system can be regarded to construct a heterocyclic 12π electrons cross conjugation system.[1] As a series of our research on the cycloaddition reactions of heterocumulenes, we have published on the synthetic approaches to this system.[2] We also have pointed out a good possibility of this system to be converted to organic electroconductors.[3]

Recently, we reported on the electrochemistries of seven-membered heterocyclic compounds; azepine and diazepine derivatives, to proceed ring opening or ring contraction reactions.[4] These facts prompted us to investigate the electrochemistry of 1. Here, the results are discussed.

A solution of 1-phenyl-3-*p*-chlorophenyl-1,3-diazadihydroazulanone (1a) in anhydrous acetonitrile was electrochemically reduced in the presence of tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte with a platinum gauze as a cathode and a platinum wire as an anode at −1.0 V vs. Ag/Ag$^+$ at O° C under a nitrogen stream. After evaporation of the solvent, the reaction mixture was column and thin layer chromatographed on silica gel to give a 1,3-hydrogen migration product (2a) and a 1,5-hydrogen migration product (3a) in 41 and 26 % yields, respectively, accompanied by 2 % amount of a recovery of the starting material.[5] The current efficiency was 58 %.

The analogous reaction of 1-phenyl-3-*p*-bromophenyl-1,3-diazadihydroazulanone (**1b**) gave the corresponding products (**2b**) (36 %) and (**3b**) (19 %), and the recovery of **1b** (6 %) (current efficiency, 83 %). The reaction of 1-phenyl-3-*p*-methylphenyl-1,3-diazadihydroazulanone (**1c**) afforded **2c** (23 %), **3c** (13 %), and a considerable amount of the recovery of **1c** (39 %) (current efficiency, 93 %). The recovery of the starting material further increased when 1-phenyl-3-*p*-methoxyphenyl-1,3-diazadihydroazulanone (**1d**) was electrochemically reduced. Thus, the reaction of **1d** afforded **2d** (9 %), **3d** (7 %), and the recovery of **1d** (77%) (current efficiency, 42 %). The interconversion between **2** and **3** was observed. Thus, compound (**2d**) was electrochemically reduced at –1.4 V vs. Ag/Ag$^+$ to give **3d** in 62 % yield, and also **3c** was reduced to **2c** in 14% yield. The structures of the products were deduced based on their spectral, especially NMR spectral properties and confirmed by the good resemblances of these properties to those of the analogous compounds.[3,6]

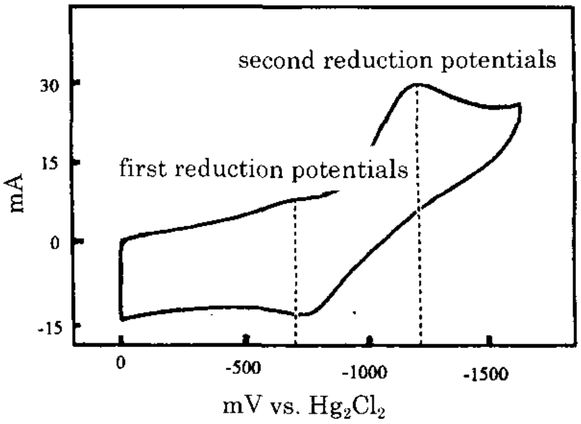
On the other hand, electrochemical oxidation of **1** in the analogous reaction conditions but under several positive electric potentials failed to afford any isolable materials but gave only a resinous intractable material.

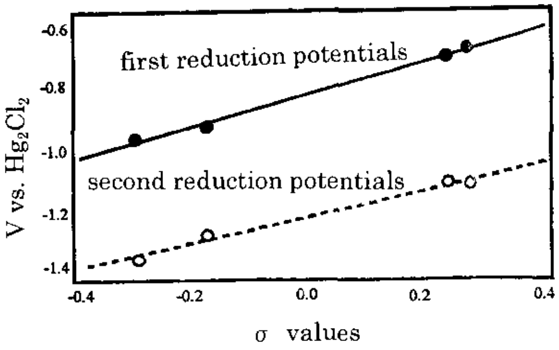


a: X=Cl, b: X=Br, c: X=Me, d: X=OMe

The total product yields (summation of the yields of **2** and **3**) seem to increase (**a**, Cl, 67 %; **b**, Br, 42 %, **c**, Me, 36 %, **d**, OMe, 16 %) with increasing of the electron withdrawing ability of the substituents at the phenyl group at 3-position.

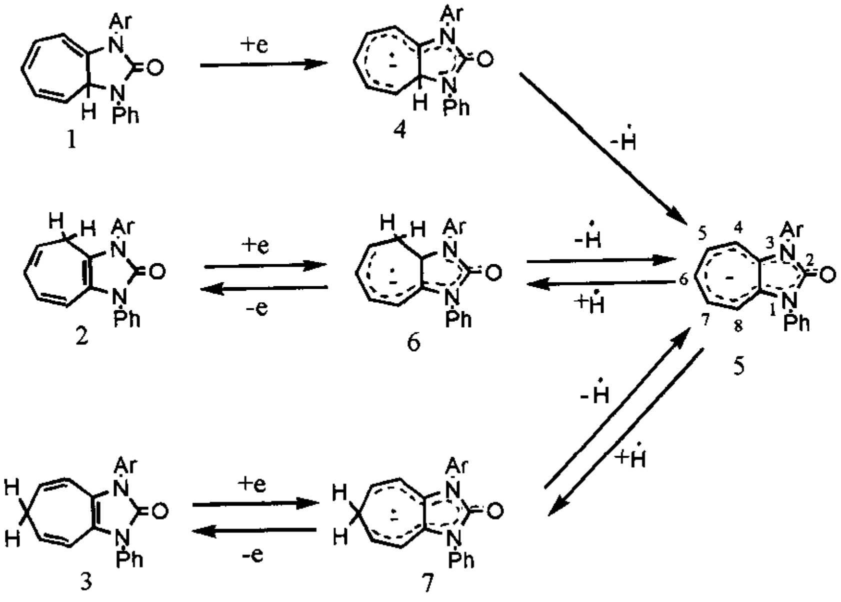
In order to investigate the relationship between these yields and the ability of electron acceptance of **1**, the reductive potentials of **1** were measured with a cyclic voltammetry.[7] As shown in the following figure, the cyclic voltammogram of **1a** shows two successive reduction potentials at –0.69 (first reduction potential) and –1.39 V (second reduction potential) vs. SCE. The relationship between the reduction potentials of **1** and the Hammett's σ values of the substituents gave a fairly good linearity as shown in the following figure. The dependence of the reduction potential on the substituent of the phenyl group at 3-position well indicates that the nitrogen atom at 3-position is included in the π-network of **1**.



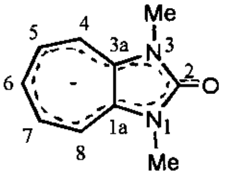


The large negative value of the reduction potentials of **1d** suggests that the electrochemical reduction of **1d** might proceed more effectively by the use of a lager negative electric voltage. The electrochemical reduction of **1d** at −1.4 V vs. Ag/Ag^+ gave improved yields of **2d** (35 %) and **3d** (15 %), together with the recovery of **1d** (45%), with a current efficiency of 70 %.

At now, the detailed reaction mechanism is not sufficiently clear, but the following mechanism is tentatively suggested. One electron acceptance of 1 from the electrode generates an anion radical intermediate (**4**), which removes a hydrogen radical to form an anion intermediate (**5**). A recombination of the hydrogen radical at 4-position of **5** (1,3-hydrogen migration) forms an anion radical intermediate (**6**), and a recombination at 6-position of **5** (1,5-hydrogen migration) forms an another type of anion radical intermediate (**7**). The following oxidations of **6** and **7** can form the products (**2**) and (**3**), respectively.[8]



The fact that the reduction of **2** or **3** do not form **1** demonstrates that only the reaction path to form **5** from **4** is irreversible. Free valences of the anion intermediate (**5**) reasonably explain this. The free valences of **5** calculated by PM3 method using a simplified model (**8**) are shown below. The value at 1a-position is apparently smaller than those at 4- or 6-positions suggesting a small possibility of the recombination of the hydrogen radical at the 1a-position of **5** to reform **1**.[7]



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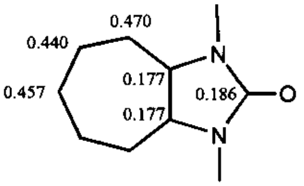

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3. K. Ito and K. Saito, *Heterocycles*, 1994, **38**, 2691; *idem, ibid.*, 1995, **41**, 2307.
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5. The typical physical properties of the products are as follows: **2c**: HRMS m/z: 314.1440. Calcd for $C_{21}H_{18}N_2O$: 314.1418. MS m/z (rel intensity): 314 (100, M^+), 313 (47), 300 (76), 271 (6). IR (KBr): 1714, 1600, 1501, 1400 cm^{-1}. ^{1}HNMR ($CDCl_3$) δ ppm: 2.38 (s, 3H), 2.95 (d, 2H, J=10.5 Hz), 5.30-5.50 (m, 1H), 6.05-6.43 (m, 3H), 7.20-7.50 (m, 9H). **3c**: HRMS m/z: 314.1419. Calcd for $C_{21}H_{18}N_2O$: 314.1418. MS m/z (rel intensity): 314 (100, M^+), 313 (41), 300 (26), 256 (5). IR (KBr): 1707, 1597, 1518, 1392 cm^{-1}. ^{1}HNMR ($CDCl_3$) δ ppm: 2.38(s, 3H), 2.55 (t, 2H, J=9.0 Hz), 5.00-5.40 (dt, 2H, J=9.0 and 7.5 Hz), 6.12 (d, 2H, J=7.5 Hz),7.20-7.50 (m, 9H). Anal. Calcd for $C_{21}H_{18}N_2O$: C, 80.20; H, 5.77; N,8.95. Found: C, 80.08; H, 5.42; N, 8.85.
6. K. Ito, K. Saito, and K. Takahashi, *Heterocycles*, 1991, **32**, 1117; K. Ito, Y. Hara, R. Sakakibara, and K. Saito, *ibid.*, 1995, 41, 1675.
7. The authors are indebted to Prof. Yoshiro Yamashita of Institute for Molecular Science for measurements of cyclic voltammetries and for MO calculations.
8. There is a possibility of a reversible 1,3-hydrogen migration between **6** and **7**. A 1,3-hydrogen migration on cycloheptatriene moieties has been reported to proceed in a basic media.
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