HETEROCYCLES, Vol. 51, No. 8, 1999

# PHOTOREACTIONS OF *N*-TOSYLDIHYDRODIAZAAZULANONES TO FORM DIAZAAZULANONES AND IONIC PAIRS BETWEEN *p*-TOLUENESULFONATE ANION AND TROPYLIUM IONS

Tadayuki Doi, Hiroyuki Ishiguro, Michie Sato, and Katsuhiro Saito*

Department of Applied Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

Abstract – Low pressure mercury lamp irradiations of *N*-aryl-*N'*-tosyldihydrodiazaazulanones in acetonitrile afforded the corresponding *N*-aryldiazaazulanones. Analogous photoreactions but using tetrahydrofuran as a solvent gave ion pairs between *p*-toluenesulfonate (tosylate) anion and the corresponding tropylium ions. The reactions are considered to proceed *via* bond cleavage between the nitrogen atoms and the tosyl groups to form ionic intermediates, which leave tosylate anions and protons to form the diazaazulanone derivatives or give the ion pairs *via* hydrogen transfers.

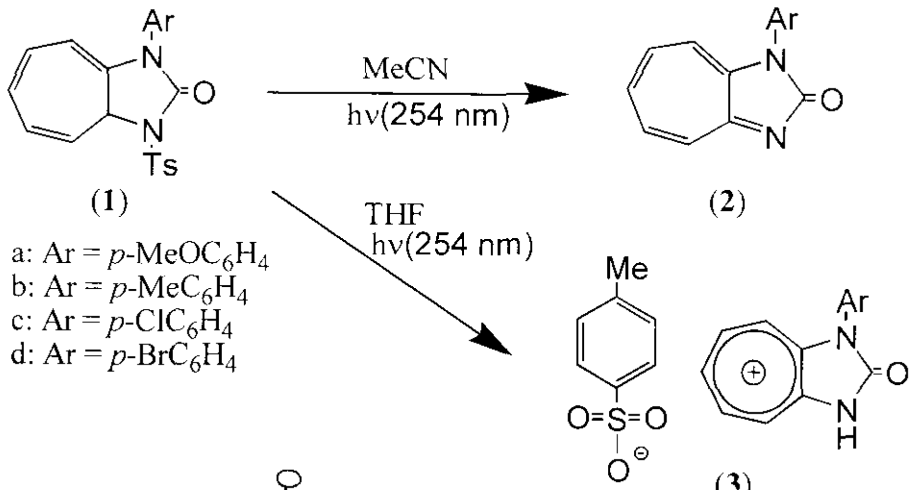
The dihydrodiazaazulanone system (1) can be considered to be constructed from a cycloheptatriene (tropilidene) moiety and a diazacyclopentanone moiety. These two moieties combined each other to form a cross conjugated $\pi$-system, containing a cyclic triene system, a carbonyl group, and two sp$^2$ hybridized nitrogen atoms. The existence of the long delocalized system is supported by the UV spectrum, which has two absorption maxima at *ca.* 250 nm (log $\varepsilon$ = 4.5) and *ca.* 310 nm (log $\varepsilon$ = 3.5).[1] This characteristic in construction of 1 prompted us to investigate a photoreaction of 1. The photoreaction of tropilidene system has long been researched extensively and 1,7-hydrogen shift and/or 4$\pi$ ring construction reactions were made clear to occur.[2] However, the tropilidene system contained in 1 is different from the ordinal tropilidene, and is expected to behave as a unit of the long conjugated system. As a series of our research on the reactivities of azaazulanone and dihydrodiazaazulanone systems, we investigated a photoreaction of the system (1).[3] Here the result is reported.

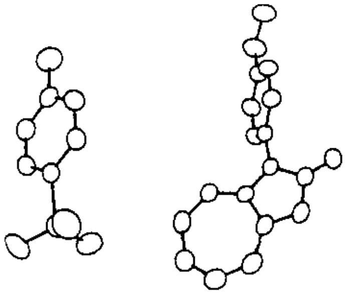
An anhydrous acetonitrile solution of *N*-(*p*-methoxyphenyl)-*N'*-tosyldihydrodiazaazulanone (1a) (24 mmol/L) was photoirradiated for 4 hours using a low pressure mercury lamp (2537 Å) under a nitrogen stream. The reaction mixture was preparative thin layer chromatographed on silica gel using ethyl acetate as a developing solvent to give light yellow crystals of *N*-(*p*-methoxyphenyl)-1,3-diazaazulanone (2a, 44.7 %, Rf= 0.1).

An analogous irradiation of a tetrahydrofuran solution of **1a** (12 mmol/L) for 4 hours afforded an ion pair (3a) (58.0 %) as pale yellow crystals, which was deposited from the reaction solution.[4]

The same type of irradiations of *N*-(*p*-methylphenyl)-*N'*-tosyldihydrodiazaazulanone (1b), *N*-(*p*-chlorophenyl)-*N'*-tosyldihydrodiazaazulanone (1c) and *N*-(*p*-bromophenyl)-*N'*-tosyldihydrodiazaazulanone (1d) in acetonitrile and tetrahydrofuran afforded *N*-(*p*-methylphenyl)-1,3-diaza-azulanone (2b, 33.2%), an ion pair (3b, 34.9%) , *N*-(*p*-chlorophenyl)-1,3-diazaazulanone (2c, 53.2%), an ion pair (3c, 52.1%) , *N*-(*p*-bromophenyl)-1,3-diazaazulanone (2d, 60.4%), and an ion pair (3d, 53.4%) , respectively.

The structure of 2 was deduced from its spectral properties and confirmed by the coincidences of these to those of an authentic sample.[1] The structure of 3 was also deduced from its spectral properties and confirmed by single crystal X-Ray analysis.[5]





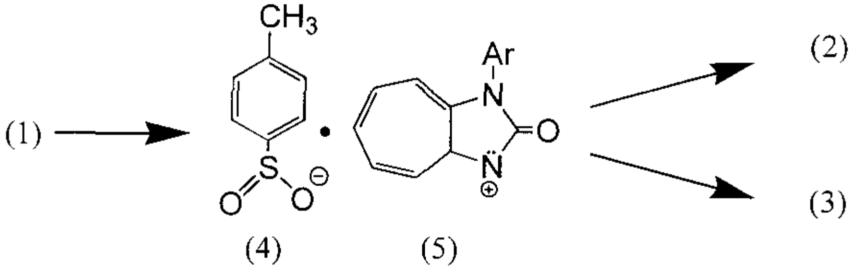
ORTEP drawing of the crystal structure of 3a

Irradiations of 1a in several solvents except tetrahydrofuran, gave almost the same results as those in acetonitrile to form the product (2a) in following yields (acetone, 52.4 %; ethanol, 31.3 %; DMSO, 66.7 %).

A conversion of 3 to 2 under the photo-irradiation conditions was observed. A low pressure mercury lamp irradiation of an anhydrous acetonitrile solution of 3c (6 mmol/L) for 30 hours afforded 2c in 59.8 % yield. However, this result does not suggest the formation of 2 in the reaction of 1 to proceed *via* 3, because in a short time irradiation (2 hours) of 3c, 2c was not detected. Considering the good yield of 2c (50.0 %) from 1c in an irradiation for 2 hours, this result tells 2 to be a primary product from 1.

The dependence of the products on the solvents used is considered to be attributed to the differences of polarities of the solvents. Several data concerning the polarities of the solvents are shown in references.[6]

The reaction is considered to proceed as follows. An ionic bond cleavage between a nitrogen atom and a tosyl group generates an ionic intermediate, which is constructed from *p*-toluenesulfinate anion (4) and dihydrodiazaazulanone cation (5) bearing the charge on a nitrogen atom.[7]



In high polar solvents (acetonitrile, DMSO, etc.), the cationic part (5) exists apart from the anionic part (4). A removal of a proton from 5 can form a diazaazulanone derivative (2), which has a stability as a member of nonbenzenoid aromatics.

On the other hand, in a low polar solvent (THF), the ionic intermediate remains as an ion pair between 4 and 5. A migration of a hydrogen atom at 7-position of the tropilidene moiety of 5 to the cationic nitrogen atom generates a stable tropylium ion type cation in the ion pair (3).

The anionic part of 3 is *p*-toluenesulfonate anion, which is considered to be formed from 4. It is known that 4 is unstable and easily oxidized to *p*-toluenesulfonate anion. Actually the formation of 3 from 1 under an oxygen stream or in a wet solvent proceeded more smoothly.[8]

## ACKNOWREDGEMENT

The authors are indebted to Prof. Hideki Masuda of Nagoya Institute of Technology for his measurement of single crystal X-ray analysis.

## REFERENCES AND NOTES

1. K. Ito, K. Saito, S. Takeuchi, and K. Takahashi, *Heterocycles*, 1992, **34**, 1415.
2. O. L. Chapman and G. W. Borden, *Proc. Chem. Soc.*, **1963**, 211; A. P. ter Borg and H. Kloosterziel, *Rec. Trav. Chim. Pays-Bus*, 1965, **84**, 241; R. W. Murray and M. L. Kaplan, *J. Am. Chem. Soc.*, 1966, 88, 3527; S. L. Mattes and S. Farid, *J. Am. Chem. Soc.*, 1983, **105**, 1386; G. C. Calhoun and G. B. Schuster, *J. Am. Chem. Soc.*, 1984, **106**, 6870.
3. K. Ito, Y. Hara, R. Sakakibara, and K. Saito, *Heterocycles*, 1995, **41**, 1675; K. Ito, K. Saito, and K. Takahashi, *Heterocycles*, 1993, **36**, 1459.

4. The physical properties of **3a** are as follows.
   mp 117-118℃. MS m/z (rel intensity). 252 (100, $M^+$ of **2a**), 237 (64), 221 (8), 210 (8), 133 (95). $^1$H-NMR ($CDCl_3$) $\delta$ ppm. 2.32 (3H, s), 3.87 (3H, s), 7.09 (2H, d, J=9.2Hz), 7.12 (2H, d, J=9.6 Hz), 7.40 (2H, d, J=9.6 Hz), 7.70 (2H, d, J=9.2 Hz), 7.86 (1H, d, J=11.5 Hz), 8.06 (1H, dd, J=11.5 and 11.5 Hz), 8.18 (1H, dd, J=11.5 and 11.5 Hz), 8.44 (1H, dd, J=11.5 and 11.5 Hz), 9.07 (1H, d, J=11.5 Hz). $^{13}$C-NMR(DMSO-$d_6$) $\delta$ ppm. 20.66, 55.34, 115.21,123.56, 124.99, 125.35, 127.29, 127.93, 129.13, 137.50, 138.77, 143.88, 144.64, 148.98, 150.13, 153.76, 160.26. IR (KBr): 1745, 1211, 1043 $cm^{-1}$. UV (MeOH): 223 nm (log $\varepsilon$ ,4.43), 249 (4.36), 345 (3.85).
5. Single crystal X-Ray analysis of **3a**.
   Hydrogen is omitted for clarity. Crystal data: $C_{22}H_{20}N_2O_5S$, Fw= 424.48, tri-clinic, space group P-1, a= 6.0274 (3), b= 18.5347 (6), c= 18.4820 (10) Å, $\beta$ = 89.044 (4), V= 2044.01 (17) Å$^3$, Z= 2, Dc= 1.327 g $cm^{-3}$, R= 0.051, Rw= 0.067 for 6509 observed reflection.
6. The data concerning the polarities of the solvents are as follows.

| Solvent | Relative permittivity ($\varepsilon$) | Swain's parameter* | | |
|---|---|---|---|---|
| | | Polarity (A+B) | Anionic solvation ability (A) | Cationic solvation ability (B) |
| DMSO | 46.68 | 1.41 | 0.34 | 1.08 |
| $CH_3CN$ | 37.50 | 1.22 | 0.37 | 0.86 |
| EtOH | 24.30 | 1.11 | 0.66 | 0.45 |
| $(CH_3)_2CO$ | 20.70 | 1.06 | 0.25 | 0.81 |
| THF | 7.58 | 0.84 | 0.17 | 0.67 |

* C. G. Swain, R. B. Moseley, and D. E. Bown, *J. Am. Chem. Soc.*, 1955, 77, 3731.

7. K. Ogura, K. Ohtsuka, M. Nakamura, N. Yahata, K. Takahashi, and H. Iida, *Tetrahedron Lett.*, 1985, 26, 2455.
8. Photoreactions of **1b** (Ar=*p*-$C_6H_4$-Me) under a variety of conditions are as follows.

| Run | Conditions | | | | | Yield of 3b |
|---|---|---|---|---|---|---|
| | Dry THF | THF | Dry $O_2$ | $N_2$ | Time (h) | |
| 1 | | ○ | | ○ | 4 | 34.9 % |
| 2 | ○ | | | ○ | 4 | No reaction |
| 3 | ○ | | ○ | | 4 | 34.3 % |

Dry tetrahydrofuran was distilled from sodium-benzophenone ketyl radical. Dry $O_2$ was passed through 96 % $H_2SO_4$ and $CaCl_2$. The photoreaction was strongly promoted by humidity in THF (Run 1) and by oxygen (Run 3).

Received, 29th March, 1999