

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

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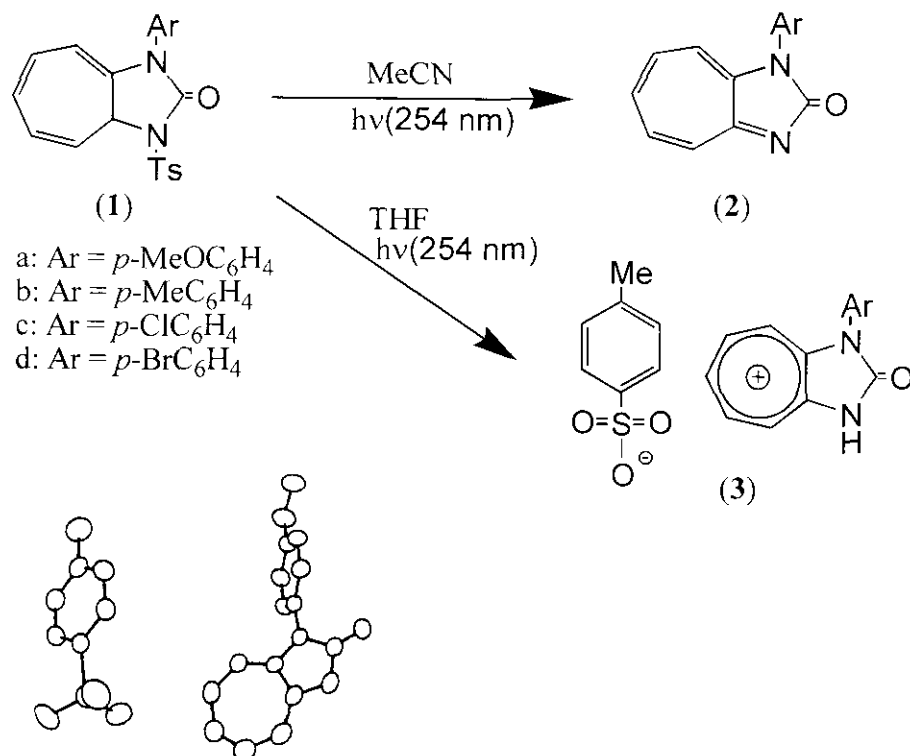
Abstract – Low pressure mercury lamp irradiations of *N*-aryl-*N'*-tosyl-dihydrodiazazulanes in acetonitrile afforded the corresponding *N*-aryldiazazulanes. Analogous photoreactions but using tetrahydrofuran as a solvent gave ion pairs between *p*-toluenesulfonate (tosylate) anion and the corresponding 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 diazazulane derivatives or give the ion pairs *via* hydrogen transfers.

The dihydrodiazazulane system (1) can be considered to be constructed from a cycloheptatriene (tropolidene) moiety and a diazacyclopentanone moiety. These two moieties combined each other to form a cross conjugated π -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 ($\log \epsilon = 4.5$) and *ca.* 310 nm ($\log \epsilon = 3.5$).¹ This characteristic in construction of 1 prompted us to investigate a photoreaction of 1. The photoreaction of tropolidene system has long been researched extensively and 1,7-hydrogen shift and/or 4π ring construction reactions were made clear to occur.² However, the tropolidene system contained in 1 is different from the ordinal tropolidene, and is expected to behave as a unit of the long conjugated system. As a series of our research on the reactivities of azaazulane and dihydrodiazazulane systems, we investigated a photoreaction of the system (1).³ Here the result is reported. An anhydrous acetonitrile solution of *N*-(*p*-methoxyphenyl)-*N'*-tosyldihydrodiazazulane (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-diazazulane (2a, 44.7 %, *R*_f = 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'*-tosyldihydrodiazazulane (1b), *N*-(*p*-chlorophenyl)-*N'*-tosyldihydrodiazazulane (1c) and *N*-(*p*-bromophenyl)-*N'*-tosyldihydrodiazazulane (1d) in acetonitrile and tetrahydrofuran afforded *N*-(*p*-methylphenyl)-1,3-diazaazulane (2b, 33.2%), an ion pair (3b, 34.9%), *N*-(*p*-chlorophenyl)-1,3-diazaazulane (2c, 53.2%), an ion pair (3c, 52.1%), *N*-(*p*-bromophenyl)-1,3-diazaazulane (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

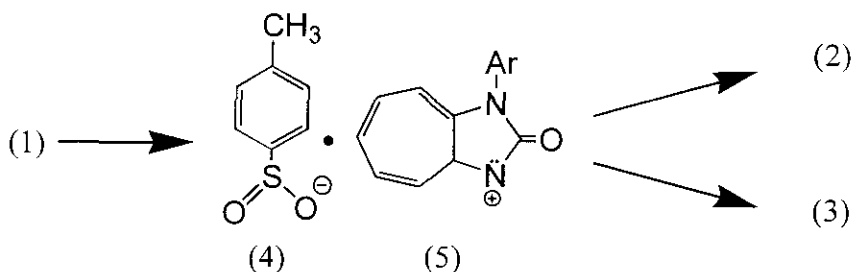
Irradiations of 1a in several solvents except tetrahydrofuran, gave almost the same results as those in acetonitrile to form the product (2a) in following yields (acetone, 52.4%; ethanol, 31.3%; DMSO, 66.7%).

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*-toluenesulfonate anion (4) and dihydrodiazazulanone 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

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4. The physical properties of 3a are as follows.

mp 117-118°C. MS m/z (rel intensity). 252 (100, M⁺ of 2a), 237 (64), 221 (8), 210 (8), 133 (95). ¹H-NMR (CDCl₃) δ 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). ¹³C-NMR(DMSO-d₆) δ 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 ε, 4.43), 249 (4.36), 345 (3.85).

5. Single crystal X-Ray analysis of 3a.

Hydrogen is omitted for clarity. Crystal data: C₂₂H₂₀N₂O₃S, Fw= 424.48, tri-clinic, space group P-1, a= 6.0274 (3), b= 18.5347 (6), c= 18.4820 (10) Å, β= 89.044 (4), V= 2044.01 (17) Å³, 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 (ε)	Swain's parameter*		
		Polarity (A+B)	Anionic solvation ability (A)	Cationic solvation ability (B)
DMSO	46.68	1.41	0.34	1.08
CH ₃ CN	37.50	1.22	0.37	0.86
EtOH	24.30	1.11	0.66	0.45
(CH ₃) ₂ CO	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.

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8. Photoreactions of 1b (Ar=*p*-C₆H₄-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 O₂ was passed through 96 % H₂SO₄ and CaCl₂. The photoreaction was strongly promoted by humidity in THF (Run 1) and by oxygen (Run 3).

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