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PHOTOREACTIONS OF 3-TOSYL- AND 6-TOSYLDIHYDRO-1,3-DIAZAAZULANONES TO FORM 1,3-DIAZAAZULANONES AND IONIC PAIRS BETWEEN *p*-TOLUENESULFONATE ANION AND 1,3-DIAZADIHYDROAZULANONE CATIONS

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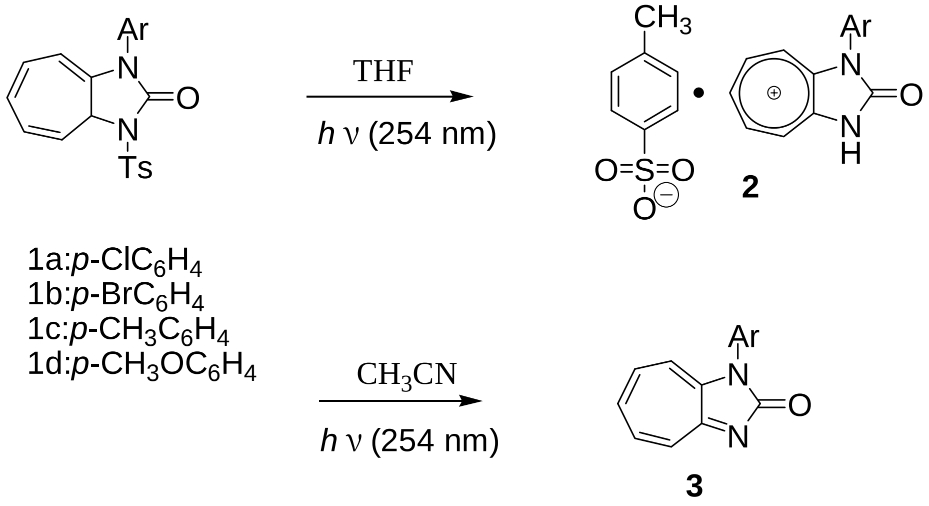
Abstract——A solvent effect was found on the photoreactions of 1-aryl-3-tosyldihydro-1,3-diazaazulanones with a low pressure mercury lamp. Thus, ion pairs between *p*-toluenesulfonate anion and the corresponding 1-aryl-1,3-diazadihydroazulanone cations were afforded by the reactions in THF. On the other hand, the corresponding 1-aryl-1,3-diazaazulanones were formed by the reactions in the other solvents. The analogous photoreactions with 1-aryl-6-tosyldihydro-1,3-diazaazulanones afforded the corresponding 1-aryl-1,3-diazaazulanones.

Not only as precursors of azulanones, a member of nonbenzenoid aromatic compounds, but also from theoretical stand point, dihydroazulanones have attracted attention of chemists. A considerable amount of papers have been published on the synthesis or elucidation of reactivities,[1] but the documents concerning the photochemistry of dihydroazulanones are few in number.[2] As a member of dihydroazulanone analogue, dihydro-1,3-diazaazulanones (**1**) have unique structural characteristics. The system of **1** is constructed from two moieties, *i.e.*, a cycloheptatirene (tropilidene) moiety and a diazacyclopentanone moiety. A combination of these two moieties generates a cross-conjugated delocalized system, composed from a cyclic triene system, a carbonyl group, and two sp^2 hybridized nitrogen atoms. The UV spectrum, which has two absorption maxima at *ca*. 250 nm ($\log \varepsilon = 4.5$) and *ca*. 310 nm ($\log \varepsilon = 3.5$) well supports the existence of this long delocalized system.[3]

The photochemistry of tropilidene system has been researched extensively to make clear the existence of 1,7-hydrogen shift and/or 4π ring contraction reactions.[4] However, considering the characteristic nature of the tropilidene moieties as a component of the system of **1**, unique behaviors in photochemistry can be expected. As a series of our study on the chemistry of azulanone and dihydroazulanone systems, we investigated photoreactions of **1**.[2] Herein, the results are reported.



Scheme1

A THF solution of 1-*p*-chlorophenyl-3-tosyldihydro-1,3-diazaazulanone (**1a**) was photoirradiated with a low pressure mercury lamp at room temperature under a nitrogen stream for 4 h. As the reaction proceeded, an ion pair (**2a**, 52 % yield) was deposited from the reaction solution as pale yellow crystals. The analogous irradiation with the diazaazulanone derivatives (**1b**, **1c**, **1d**) afforded the corresponding ion pairs (**2b**, **2c**, and **2d**) in 53, 35, and 27 % yields, respectively.

Figure 1 shows an existence of a substituent effect in the yield of **2**, *i.e.*, the electron withdrawing groups promoted the yields.

When the photoirradiation of **1** was carried out in acetonitrile, a different result from that in THF was obtained. Thus, an anhydrous acetonitrile solution of **1a** was irradiated with a low pressure mercury lamp for 4 h under the same reaction conditions as above. After evaporation of the solvent, the resulted residue was separated with thin-layer chromatography on silica gel to give 1-*p*-chlorophenyl-1,3-diazaazulanone (**3a**) in 53 % yield.

The same type reactions in acetonitrile with **1b**, **1c**, and **1d** afforded the corresponding diazaazulanone derivatives (**3b**, **3c**, **3d**) in 60, 33, and 45 % yields, respectively. The analogous substituent effects as the case of **2** were found on the yields of **3** as shown in Figure 1.

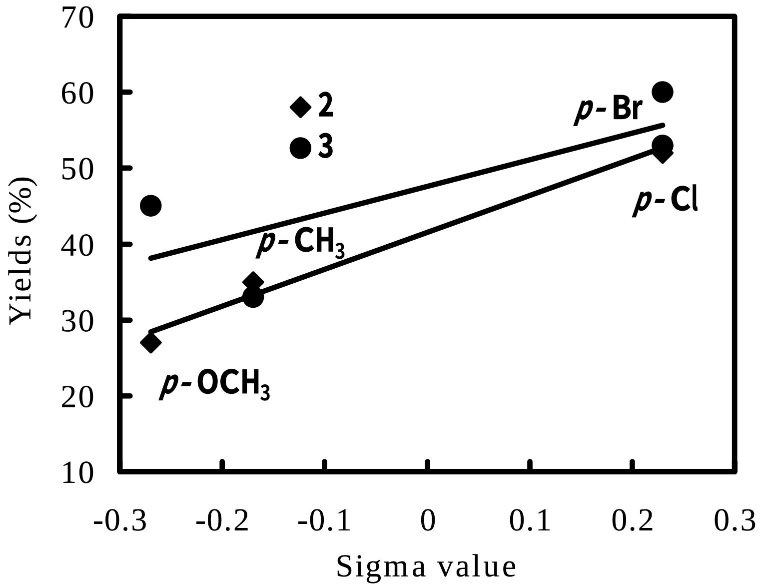


Figure 1

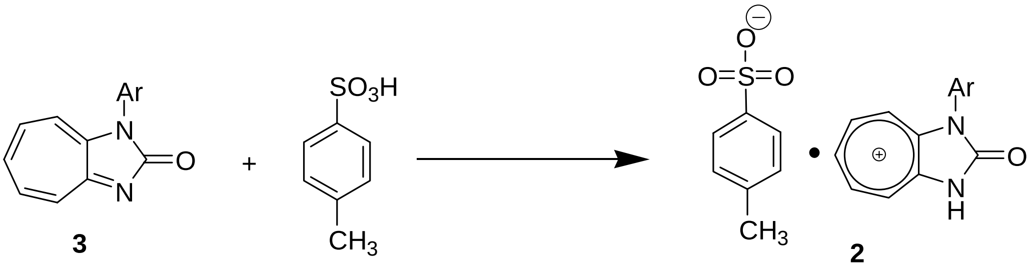
The analogous photoreactions of **1d** in the another solvents proceeded through the same path as that in acetonitrile to form **3d**. However, the yields of **3d** depended on the solvent used. The Table 1 summarizes the yields of **3d** and the dielectric constants of the solvents used suggesting that the polar solvents promoted the yield.

Table 1. Yields of **3d** and dielectric constants of the solvents

	Solvents		
	C_2H_5OH	CH_3CN	DMSO
3d	31 %	45 %	67 %
Dielectric constants	24.55	37.50	46.68

The interconversion between **2** and **3** was examined under some reaction conditions as follows. A treatment of a methanol solution of **2b** with potassium hydroxide at rt for 2 h converted **2b** to **3b** in an almost quantitative yield.

The ion pair (**2**) was formed in the reaction of **3** with an equimolar amount of *p*-toluenesulfonic acid. The reaction conditions and the yields of **2** are summarized in Table 2 with the case of **2b**.



Scheme 2

Table 2. Yields of **2b** under various conditions

Entry	Solvent	Reaction temperature	Reaction time (h)	Yields of **2b** (%)
1	THF	rt	6	23
2	THF	Reflux	6	88
3	CH_3CN	rt	6	67
4	CH_3CN	Reflux	6	90

These facts suggested the structure of **2** to be close to a complex between **3** and *p*-toluene sulfonate.

The structures of **3** were deduced on the basis of their spectral properties and confirmed by the coincidences of these properties with those of the authentic samples.[6] The structures of **2** were deduced on the basis of their spectral properties and finally decided by a single crystal X-Ray analysis.[2]

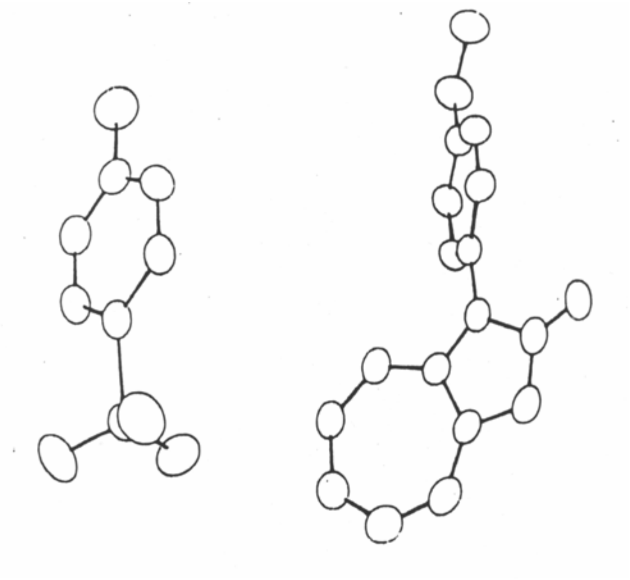
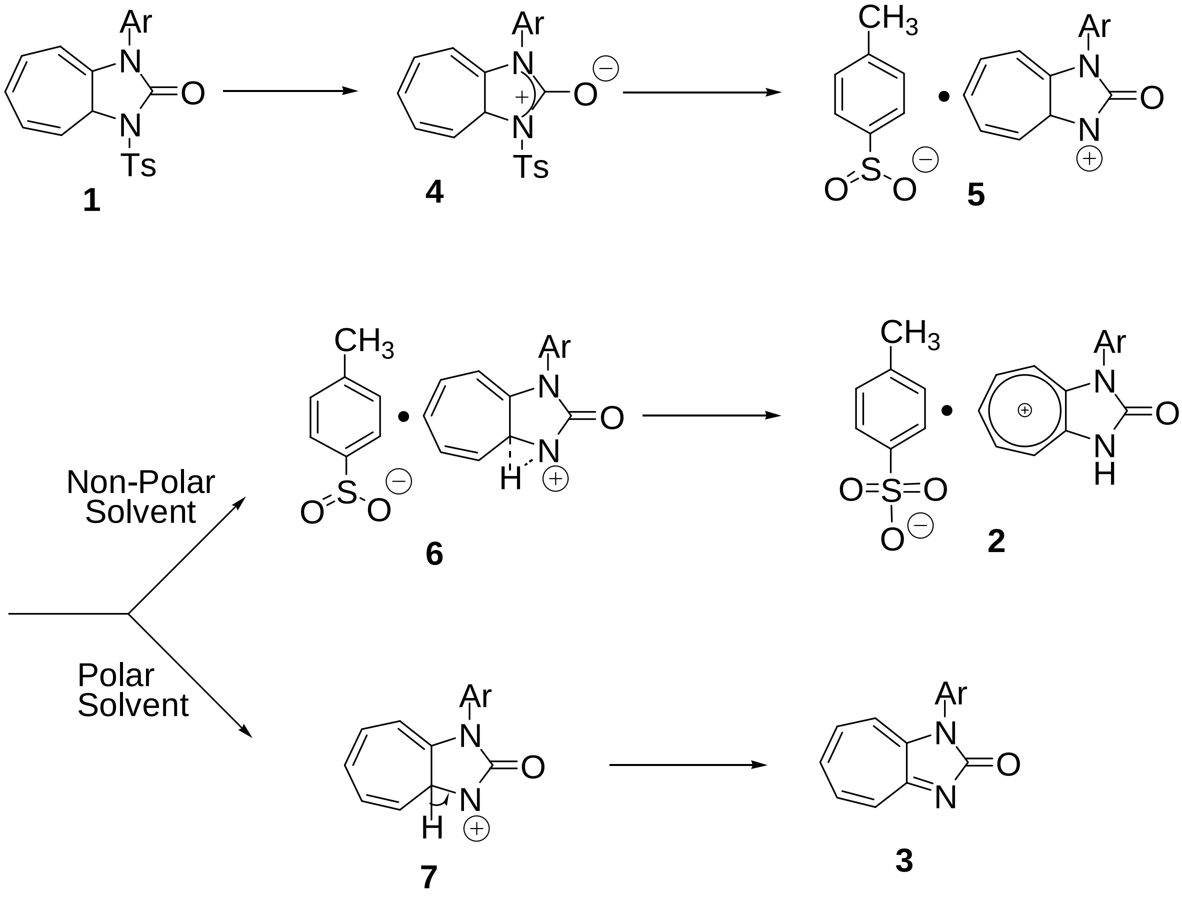
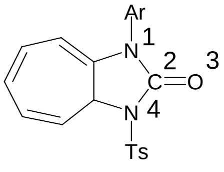


Figure 2

A photoirradiation of **2a** in acetonitrile with a low pressure mercury lamp generated **3a** in 60 % yield. However, the reaction proceeded slowly, and a prolonged photoirradiation (30 h) was required by the complete consumption of the starting material (**2a**). This fact demonstrates that **3** can be formed in the photoreaction of **2**. However, considering the difference of the reaction rate between the formation of **3** from **1** and from **2**, the formation of **3** from **1** cannot proceed through **2**.



Scheme 3



1

Table 3. Charge distribution of **1**

	Ground State	Excited State
N^1	0.1173	0.1936
C^2	0.3139	0.3011
O^3	-0.3687	-0.2842
N^4	-0.5385	-0.4750

The reaction is considered to proceed as follows. Photoirradiation of **1** generates an excited state (**4**) of **1**, which is thought to have an ionic character as shown in Scheme 3. The charge distribution of the ground state and the excited state of **1** are summarized in Table 3. In the excited state, the electron density on the heterocyclic part is diminished. This fact suggests a shift of the electron density away from N^4 to the tropilidene moiety, resulting weakening of the bond between N^4 and the tosyl group.

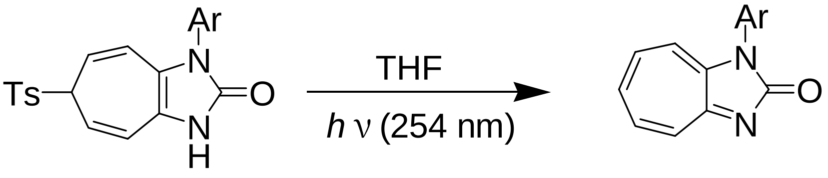
A bond cleavage between N^4 and the tosyl group generates an ionic pair intermediate (**5**). The effect of the solvents shown in Figure 1 is considered to reflect thestabilities of the tropylium ion part of the intermediate (**5**).

In the nonpolar solvent (THF) the anionic part and the cationic part of **5** remain in contact each other. A hydrogen migration in the cationic part and an appropriate oxidation of the anionic part can form the final product (**2**).

Table 4. Yields of **2b** under various reaction conditions

Entry	Dry THF	THF	Dry O_2	N_2	Reaction time (h)	Yields of **2** (%)
1		○		○	4	53
2	○			○	4	6
3	○		○		4	44

Table 4 demonstrates the yields of **2b** in the photoreactions of **1b** under various reaction conditions. In the reaction in anhydrous THF as a solvent under a nitrogen stream (Entry 2), only a small amount of **2b** was formed. On the other hand, uses of usual (wet) THF (Entry 1)or a oxygen stream (Entry 3) resulted in the formation of **2b** in considerable yields. This fact suggests that the anionic part of **5** is oxidized by water or oxygen dissolved in the solvents.



8a:p-ClC_6H_4
8b:p-BrC_6H_4
8c:p-$CH_3C_6H_4$

3a:p-ClC_6H_4
3b:p-BrC_6H_4
3c:p-$CH_3C_6H_4$

Scheme 4

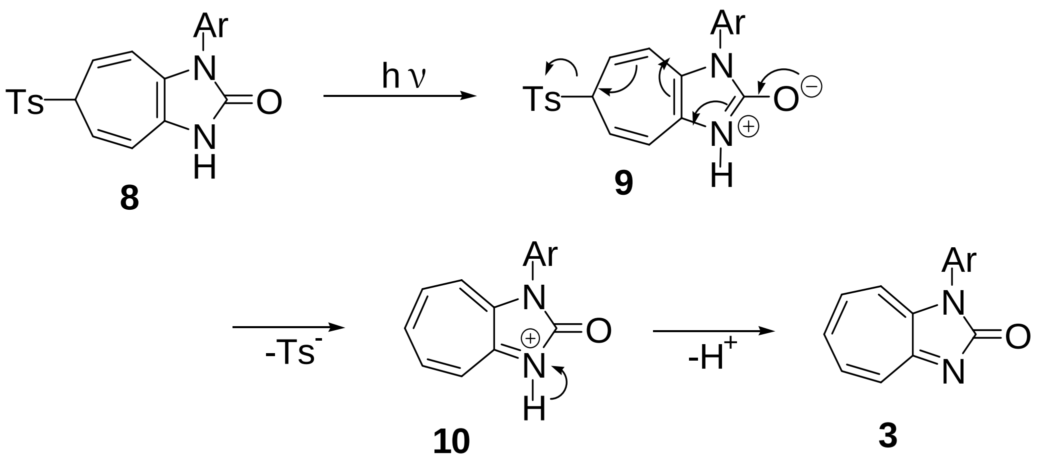
On the other hand, in polar solvents, the cationic part of **5** behaves apart from the anionic part. An elimination of hydrogen from **5** can form the final product (**3**).

Photoreactions of the isomers of **1**, 1-aryl-6-tosyl-1,3-diazadihydroazulanones (**8**) were investigated. A THF solution of 1-*p*-chlorophenyl-6-tosyl-1,3-diazadihydroazulanobne (**8a**) was irradiated with a low pressure mercury lamp at room temperature under a nitrogen stream for 3 h. The usual treatment of the reaction mixture gave **3a** in 19 % yield, which was also formed in the analogous reaction but using acetonitrile as a solvent in 32 % yield. The product yields in the reactions with some isomers of **8** are summarized in Table 5.

Table 5. Yields of **3** in the reaction of **8**

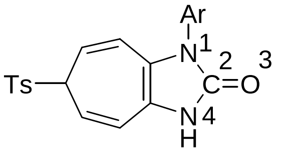
		3a	3b	3c
Yields	THF	19 % (3 h)	22 % (3 h)	17 % (3 h)
	CH_3CN	32 % (3 h)	37 % (3 h)	26 % (3 h)

The charge distributions of **8** in the ground state and in the excited state calculated with MINDO 3 method are as shown in the Table 6. In the excited state, the electron cloud seems to shift from N^4 to N^1. Considering these electron densities, the excited state of **8** is thought to have a contribution of an ionic form (**9**). The reaction is considered to proceed through an elimination of the tosyl group in **9** to form the cationic intermediate (**10**), which then removes a hydrogen to generate the final product.



Scheme 5

Table 6. Charge distribution of **8**



8

	Ground State	Excited State
N^1	0.0973	0.1349
C^2	0.1932	0.2117
O^3	-0.3788	-0.3383
N^4	0.1524	0.0806

ACKNOWREDGEMENT

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

EXPERIMENTAL

Photoirradiation was performed with six low pressure mercury lamps National GL-15 in a 50 ml quartz pear shaped flask. MS and NMR spectra were measured with Hitachi 220A and Varian GEMINI 200/300 spectrometers, respectively. IR spectra were measured with a JASCO FT/IR-5300 spectrophotometer. Wakogel C200 and B5F were used for column and thin-layer chromatography, respectively.

Only typical reactions are mentioned below.

Photoreaction of ***1a*** *in THF.* A solution of **1a** (200 mg, 0.5 mmol) in THF (20 mL) was photoirradiated with low pressure mercury lamps at rt under a nitrogen stream for 4 h. The deposited crystals were filtered off to give **2a** (102 mg, 52 %).

2a: Pale yellow crystals. mp 238-239 °C (from ethanol). Anal. Calcd for $C_{21}H_{17}N_2O_4ClS$: C, 58.81; H, 4.00; N, 6.53. Found: C, 58.67; H, 3.68; N, 6.55. MS *m/z* (rel intensity): 258 (35), 256 (100), 221 (19), 119 (80). IR (KBr): 3489, 1751, 1228, 1032 cm^{-1}. ^{1}H NMR (DMSO- d_6), δ: 2.28 (s, 3 H), 7.10 (d, 2 H, J = 8.5 Hz, tosyl), 7.46 (s, 2 H, tosyl), 7.65 (d, 2 H, J = 7.5 Hz aryl), 7.80 (d, 2H, aryl), 8.08 (d, 1H, J = 9.7 Hz), 8.27 (dd, 1H, J = 9.7 and 9.7 Hz), 8.42 (dd, 1H, J = 9.7 and 9.7 Hz), 8.46 (d, 1H, J = 9.7 Hz), 8.58 (dd, 1H, J = 9.7 and 9.7 Hz).

2b: Pale yellow crystals. mp 238-239 °C (from ethanol). Anal. Calcd for $C_{21}H_{17}BrS$: C, 53.29; H, 3.62; N, 5.92. Found: C, 52.75; H, 3.47; N, 5.99. MS *m/z* (rel intensity): 302 (83), 300 (81), 221 (26), 119 (100). IR (KBr): 3443, 1749, 1226, 1032 cm^{-1}. ^{1}H NMR (DMSO- d_6), δ: 2.28 (s, 3 H), 7.10 (d, 2 H, J = 8.5 Hz, tosyl), 7.46 (s, 2 H, tosyl), 7.58 (d, 2 H, *J* = 7.5 Hz, aryl), 7.92 (d, 2H, aryl), 8.08 (d, 1H, *J* = 9.7 Hz), 8.27 (dd, 1H, *J* = 9.7 and 9.7 Hz), 8.42 (dd, 1H, *J* = 9.7 and 9.7 Hz), 8.46 (d, 1H, *J* = 9.7 Hz), 8.59 (dd, 1H, *J* = 9.7 and 9.7 Hz).

2c: Pale yellow crystals. mp 183-184 °C (from ethanol). MS *m/z* (rel intensity): 235 (100), 221 (33), 194 (9), 119 (76). IR (KBr): 3491, 1747, 1234, 1043 cm^{-1}. ^{1}H NMR (DMSO-d_6), δ: 2.30 (s, 3 H), 2.45 (s, 3 H), 7.10 (d, 2 H, *J* = 8.5 Hz, tosyl), 7.48 (d, 2 H, tosyl), 7.50 (s, 4 H, aryl), 7.95 (d, 1 H, *J* = 9.7 Hz), 8.20 (dd, 1 H, *J* = 9.7 and 9.7 Hz), 8.36 (dd, 1 H, *J* = 9.7 and 9.7 Hz), 8.40 (d, 1 H, *J* = 9.7 Hz), 8.52 (dd, 1 H, *J* = 9.7 and 9.7 Hz).

2d: Pale yellow crystals. mp 117-118 °C (from ethanol). MS *m/z* (rel intensity): 252 (100), 237 (64), 221 (8), 210 (8), 133 (95). IR (KBr): 3458, 1745, 1230, 1026 cm^{-1}. ^{1}H NMR (DMSO-d_6), δ: 2.30 (s, 3 H), 3.88 (s, 3 H), 7.11 (d, 2H, *J* = 8.5 Hz, tosyl), 7.24 (d, 2 H, *J* = 7.5 Hz, aryl), 7.45 (d, 2H, tosyl), 7.53 (d, 2 H, aryl), 8.05 (d, 1H, *J* = 9.7 Hz), 8.28 (dd, 1H, *J*=9.7 and 9.7 Hz), 8.45 (dd, 1H, *J* = 9.7 and 9.7 Hz), 8.50 (d, 1H, *J* = 9.7 Hz), 8.60 (dd, 1H, *J* = 9.7 and 9.7 Hz).

*Photoirradiation of **1a** in acetonitrile*. A solution of **1a** (127 mg, 0.31 mmol) in acetonitrile (20 mL) was photoirradiated with low pressure mercury lamps at rt under a nitrogen stream for 4 h. After evaporation of the solvent the residue was thin-layer chromatographed on silica gel to give **3a** (42 mg, 53 %, ethyl acetate, R_f = 0.1).

*Photoirradiation of **4b** in acetonitrile*. A solution of **4b** (67 mg, 0.17 mmol) in THF (15 mL) was photoirradiated with low pressure mercury lamps at rt under a nitrogen stream for 3 h. After evaporation of the solvent the residue was thin-layer chromatographed on silica gel to give **3b** (7 mg, 17 %, ethyl acetate, R_f = 0.1).

*Reaction of **2b** with potassium hydroxide*. A solution of **2b** (34 mg, 0.07 mmol) and potassium hydroxide (106 mg, 1.9 mmol) in methanol (30 mL) was stirred at rt for 2 h. After addition of brine the reaction mixture was extracted with methylene chloride. After the usual treatment the solvent was evaporated to give crystals of **3b** (22 mg, *ca.* 100 %).

*Photoreaction of **2a***. A solution of **2a** (39 mg, 1 mmol) in acetonitrile (15 mL) was irradiated with a low-pressure mercury lamp at rt under a nitrogen stream for 30 h. After evaporation of the solvent, the residue was thin-layer chromatographed on silica gel to give **3a** (25 mg, 60 %). In a short time irradiation (2 h), formation of **3a** was not obvious. *Reaction of **3b** with p-toluenesulfonic acid*. A solution of **3b** (142 mg, 0.47 mmol), *p*-toluenesulfonic acid (84 mg, 0.49 mmol) in THF (20 mL) was stirred at rt for 6 h. After evaporation of the solvent, the residue was column chromatographed on silica gel to give **2b** with an eluant of ethyl alcohol (51 mg, 23 %).

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