Photo-Stevens rearrangement reaction of *S*-naphthylmethyl-*N*-*p*-tosylsulfimides

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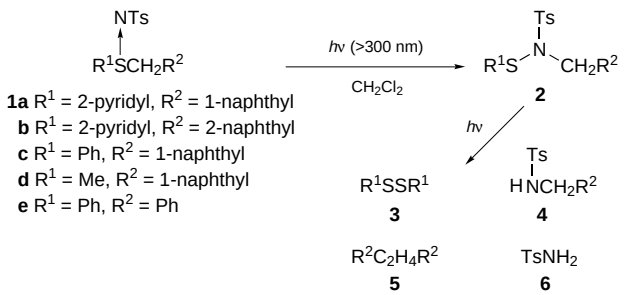
Photolysis sulfimides unexpectedly led to Stevens rearrangement products.

In the thermal reaction of sulfimides, the products derived *via* Stevens rearrangement were reported to be formed.[1] In the photolysis of sulfimides, however, it is reported that nitrenes are initially generated *via* a photo-induced cleavage of the S–N linkage.[2] In contrast to this mechanistic route for photolytic decomposition of sulfimides, another route *via* Stevens rearrangement was recently reported for the particular case of a cyclic sulfimide derivative, *i.e.* *N*-tosylnaphtho[1,8-*de*]-1λ⁴,3-dithiin-1-imine, which rearranged to naphtho[1,8-*ef*]-[1,4,2]dithiaazepine, followed by de-imination to give *N*-*p*-tosylaldimines and naphtho[1,8-*cd*]-1,2-dithiole quantitatively.[3] In this reaction the driving force apparently results from formation of a stable cyclic disulfide *via* the through-space interaction between the two sulfur atoms at the 1,8-positions of naphthalene.

In order to study more precisely and photolytic behaviour of acyclic sulfimide derivatives, we prepared several *S*-naphthylmethyl-*N*-*p*-tosylsulfimides and carried out their photolysis using a high-pressure mercury lamp with a Pyrex filter under nitrogen.† When **1a**‡ was irradiated in degassed MeOH under these conditions, the major products were dipyridyl disulfide **3a** and *N*-(naphthylmethyl)toluene-*p*-sulfonamide **4a**.§ In view of the formation of **4a**, the reaction is considered to pass through a rearrangement mechanism, *i.e.* a Stevens-type rearrangement as depicted in Scheme 1. Here we report the first examples of this photo-induced Stevens rearrangement reaction in *S*-naphthylmethyl-*N*-*p*-tosylsulfimide derivatives.

S-Aryl- or *S*-alkyl-*S*-naphthylmethyl-*N*-*p*-tosylsulfimides **1a**–**e** were prepared by the reaction of the corresponding sulfides with the sodium salt of *N*-chlorotoluene-*p*-sulfonamide (Chloramine T) in MeCN in high yields. Photolysis of *S*-naphthylmethyl-*N*-*p*-tosylsulfimides in degassed CH_2Cl_2 was carried out under the previously described conditions for 2 h. The results are summarized in Table 1. The photolyses of *S*-pyridyl-, *S*-phenyl- and even *S*-methyl-*S*-(1-naphthylmethyl)- or *S*-(2-naphthyl-methyl)-*N*-*p*-tosylsulfimide derivatives **1a**–**d** (entries 1–4) were found to lead to the Stevens rearrangement product **2**, as well as **3** and **4**, which are formed by photolysis of **2** in a secondary photochemical step, while in the photolysis of *S*-benzyl-*S*-phenyl-*N*-*p*-tosylsulfimide **1e** (entry 5), the reaction



Scheme 1

did not proceed at all. This result suggests that a napthyl group is necessary in this reaction as a useful chromophore to accept photoirradiation and to initiate the photoreaction. Therefore, measurements of the UV–VIS spectra of **1a**–**d** were carried out and showed, as expected, the existence of a strong absorption band ($\log\varepsilon = 4.9$) around 230 nm, extending beyond the 300 nm region as shoulders, while **1e** showed no absorption beyond 300 nm.

A further study of the photolysis of *S*-(2-pyridyl)-*S*-(1-naphthylmethyl)-*N*-*p*-tosylsulfimide **1a** in several solvents was carried out under the same conditions. The products formed were found to depend significantly on the nature of solvents used. In aprotic solvents such as CH_2Cl_2 and MeCN, the primary rearranged product **2a**¶ was formed as the major product; however, in acetone the secondary products **3a** and **4a** were the major products, presumably due to acceleration of the photochemical excitation of **2a** by probable triplet sensitization of acetone, as suggested by Guo and Jenks in the photolysis of sulfoxide.[4] Meanwhile, in alcoholic solvents, another mechanistic path is apparently involved and toluene-*p*-sulfonamide **6**, as well as the products **3a** and **4a** *via* Stevens-type rearrangement, was formed predominantly. One possibility for this mechanism is the nitrene pathway, which would immediately lead to sulfonamide **6** and the corresponding sulfide, which is observed to decompose to **3a** and **5a** under the same conditions. Another possibility is a pathway involving the initial protonation at the iminonitrogen atom of the sulfimide and subsequent

Table 1 Photolysis of *N*-tosylsulfimides **1** in CH_2Cl_2[a]

			Yield (%)[b]		
Entry	Compound	Conversion (%)	**2**	**3**	**4**
1	**1a**	100	27	45	72
2	**1b**	92	47	37	46
3	**1c**	94	40	33	30
4	**1d**	63	54	—[c]	42
5	**1e**	0	—	—	—

[a] Irradiation with a 400 W high-pressure Hg lamp; concentration: 0.2 mmol; reaction time = 2 h. [b] Isolated yield. [c] Dimethyl disulfide not isolated.

Table 2 Photolysis of *S*-(2-pyridyl)-*S*-(naphthylmethyl)-*N*-*p*-tosylsulfimide **1a** in different solvents[a]

	Yield (%)[b]				
Solvent	**2a**	**3a**	**4a**	**5a**	**6**
MeOH	0	25	15	7	64
Pr^{i}OH	0	38	34	21	57
CH_2Cl_2	27	45	72	trace	0
MeCN	15	33	54	trace	0
Me_2CO	0	41	74	4	0

[a] Irradiation with a 400 W high-pressure Hg lamp: concentration: 0.2 mmol; reaction time = 2 h. Isolated yield.

formation of an alkoxysulfonium salt (counter anion $TsNH^-$) which eventually decomposes to the corresponding sulfide and a carbonyl compound.‖ A similar mechanism was suggested by Oae in the case of the thermolysis of *N*-*p*-tosylsulfimides in MeOH.[1a]

In order to confirm the mechanistic pathway of this photoreaction, the product distribution in the course of photolysis of **1a** in CH_2Cl_2 under the previously described conditions was determined by quantitative analysis with HPLC. The result is illustrated in Fig. 1; the amount of starting sulfimide **1a** decreased gradually, and three new species appeared. Two were found to be di(2-pyridyl) disulfide **3a** and *N*-(1-naphthylmethyl)toluene-*p*-sulfonamide **4a** by comparing their HPLC retention times and their spectral data with those of authentic compounds prepared or separated by chromatography. The third species showed a maximum after 40 min and then gradually decreased. This probably points to the existence of the intermediate **2** in this reaction, which apparently reacted to give the products **3a** and **4a**. Therefore, the reaction mixture was separated by HPLC after 40 min photolysis and the product corresponding to this intermediate was identified as **2a**. Further, in order to clarify that **2a** is exactly the intermediate of this reaction, photolysis of **2a** thus separated was carried out under the same conditions to afford the expected products **3a** and **4a** in good yields. All these results indicate clearly that this reaction proceeds *via* a photo-induced Stevens rearrangement to afford the intermediate **2a**, which subsequently decomposes to dipyridyl disulfide **3a** and *N*-(1-naphthylmethyl)toluene-*p*-sulfonamide **4a** together with a small amount of product **5a** *via* direct cleavage of the S–CH_2 linkage.

We are now pursuing further studies to clarify the limitations and the detailed mechanism of this reaction.

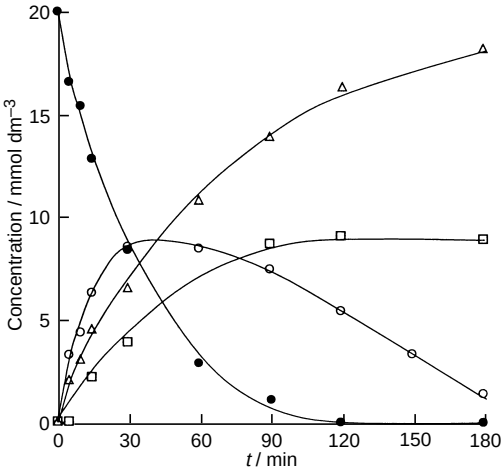


Fig. 1 Product distribution in the course of photolysis of **1a**; (●) **1a**, (○) **2a**, (□) **3a** and (△) **4a**

Footnotes

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† All photolyses were carried out in 9 mm i.d. Pyrex glass tubes, sealed with a septum under nitrogen atmosphere at room temperature, with irradiation from a 400 W high-pressure mercury lamp.

‡ Compound **1a** was prepared by the following procedure: a solution of pyridyl naphthylmethyl sulfide and Chloramine T (1.5 equiv.) in 100 ml of MeCN was refluxed for 6 h. After removal of MeCN, washing with water to remove excess Chloramine T and drying, *S*-pyridyl-*S*-naphthylmethyl-*N*-*p*-tosylsulfimide was obtained in 88% yield, mp 164 °C (AcOEt–hexane). *Selected data* for **1a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.20 (s, Me, 3 H), 4.46 (dd, *J* 13 Hz, 1 H), 5.34 (dd, *J* 13 Hz, 1 H), 6.63–6.65 (m, 2 H), 7.17–7.34 (m, 5 H), 7.48–7.58 (m, 3 H), 7.75–7.84 (m, 2 H), 7.97–8.08 (m, 2 H), 8.31–8.33 (m, 1 H), 8.70–8.72 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 54.8, 122.1, 122.9, 123.7, 125.1, 125.5, 125.7, 126.1, 127.0, 127.8, 128.8, 128.8, 129.5, 130.0, 131.2, 131.3, 133.6, 138.9, 140.8, 149.9; ν_{max} (KBr)/cm^{-1} 1280, 1100 (SO_2), 980 (SN); Calc. for $C_{23}H_{20}N_2O_2S_2$: C, 65.68; H, 4.79; N, 6.66. Found: C, 65.52; H, 4.84; N, 6.49%.

§ *Selected data* for **4a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.45 (s, Me, 3 H), 4.53 (d, *J* 1 Hz, CH_2, 2 H), 4.63 (d, *J* 2 Hz, NH, 1 H), 7.25–7.35 (m, 4 H), 7.46–7.51 (m, 2 H), 7.77–7.90 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$); δ 21.5, 45.4, 123.2, 125.1, 126.0, 126.7, 126.9, 127.2, 128.7, 129.1, 129.7, 131.1, 133.7, 136.4, 143.5; ν_{max} (KBr)/cm^{-1} 1330, 1160 (SO_2), 3300 (NH); *m/z* 311 (M^+); Calc. for $C_{18}H_{17}NO_2S$: C, 69.42; H, 5.50; N, 4.49. Found: C, 69.51; H, 5.62; N, 4.33%.

¶ *Selected data* for **2a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, Me, 3 H), 6.70—6.73 (m, 1 H), 6.81–6.83 (m, 1 H), 6.99–7.03 (m, 1 H), 7.30–7.36 (m, 3 H), 7.47–7.49 (m, 1 H), 7.57–7.61 (m, 1 H), 7.65–7.67 (d, *J* 2 Hz, 1 H), 7.74–7.76 (d, *J* 2 Hz, 1 H), 7.85–7.88 (m, 2 H), 8.08–8.10 (m, 1 H), 8.44–8.47 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 55.8, 118.3, 119.9, 123.8, 124.8, 125.7, 126.7, 127.9, 128.5, 129.3, 129.6, 129.7, 130.0, 131.9, 133.5, 135.0, 136.1, 144.3, 148.1, 160.6; ν_{max}(KBr)/cm^{-1} 1351, 1165 (SO_2); *m/z* 78 ($C_5H_5N^+$), 127 ($C_{10}H_7^+$), 141 ($C_{10}H_7CH_2^+$), 155 (Ts^+), 156 ($C_{10}H_7CH_2NH^+$), 311 ($TsNHCH_2C_{10}H_7^+$), 420 (M^+); Calc. for $C_{23}H_{20}N_2O_2S_2$: C, 65.68; H, 4.79; N, 6.66. Found: C, 65.86; H, 4.79; N, 6.60%. The methylene protons ($CH_2C_{10}H_7$) were not observed in the ^{1}H NMR spectrum, even after varying the solvent, although all other analytical and combustion data confirmed this structure.

‖ In MeOH the formation of paraformaldehyde was observed.

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