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A new photochemical ring expansion of 1,2-benzisothiazole 1,1-dioxides

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Abstract—A new facile photoconversion of 1,2-benzisothiazole 1,1-dioxides into 1,3-2*H*-benzothiazine 1,1-dioxides upon 254 nm irradiation in methanol or acetonitrile is reported. © 2001 Elsevier Science Ltd. All rights reserved.

Considerable attention has been focused on the photochemistry of five-membered heterocyclic ring systems.[1] By far the greatest area of activity in this field has been a study of the photoisomerization of the heterocyclic nucleus. The literature on the photoprocesses observed with isothiazoles has recently been reviewed.[1,2] The photoisomerization of various 1,2-benzisothiazoles[1a] has also been studied in our laboratory,[3–6] as well as by others[7–9] and these studies have dealt with the synthetic usefulness as well as the reaction mode of this ring system.

The photoconversion of **1** (R^1 being methyl or phenyl) to the isomeric 2,3-dihydro-2-hydroxy-1,2-benzisothiazole 1-oxides by a formal oxygen shift from sulfur to nitrogen has been firmly established.[3–5] The hydrogen atom at nitrogen in **1** was replaced by CH_2OR ($R = CH_3$, *i*-Pr) and still the formal oxygen shift from sulfur to nitrogen does occur.[4] We wished to clarify whether a similar oxygen shift could also be possible by introducing at the *N*-methylene group an acceptor (Acc) substituent instead of a donor as in compounds **2**. Substituents CH_2-Acc would indeed have a migratory aptitude different from that of CH_2-donor groups if the rearrangement followed a polar mechanism.[5]

Thus, sultams **2** were prepared by treating starting materials **1** with primary alkyl bromides Br-CH_2-R^2 (see Table 1) in the presence of sodium hydride and 18-crown-6 (Scheme 1). When the *N*-alkylated sultams **2** were subjected to 254 nm photolysis[10] in acetonitrile or methanol for the periods listed in Table 1, a single photoproduct was obtained in all cases (except from sultam **2a**) which was demonstrated to be the 2-substituted-1,3-2*H*-benzothiazine 1,1-dioxides **3b–e**. Sultam

Table 1. Photoconversion of sultams **2** to 1,3-benzothiazines **3**

2, **3**, **4**	R^1	R^2	Period of irradiation (h)	Yield of **3** (%)[a]	Chemical shifts[c] δ (ppm)	
					H-2	C-2
a	CH_3	Ph	2	45[b]		
			6	60	5.50	72.6
b	CH_3	CO_2CH_3	2	81	5.31	71.5
c	CH_3	CN	1	86	5.27	62.0
d	CH_3	$COCH_3$	1.5	84	5.32	70.3
e	Ph	Ph	7	58	5.85[d]	74.1[d]

[a] Based on the consumed starting material.

[b] Additionally, 20% of compound **4a** have been formed.

[c] In $CDCl_3$ unless stated otherwise.

[d] In DMSO-d_6.

Keywords: photorearrangement; ring expansion; 1,2-benzisothiazoles; 1,3-benzothiazines.

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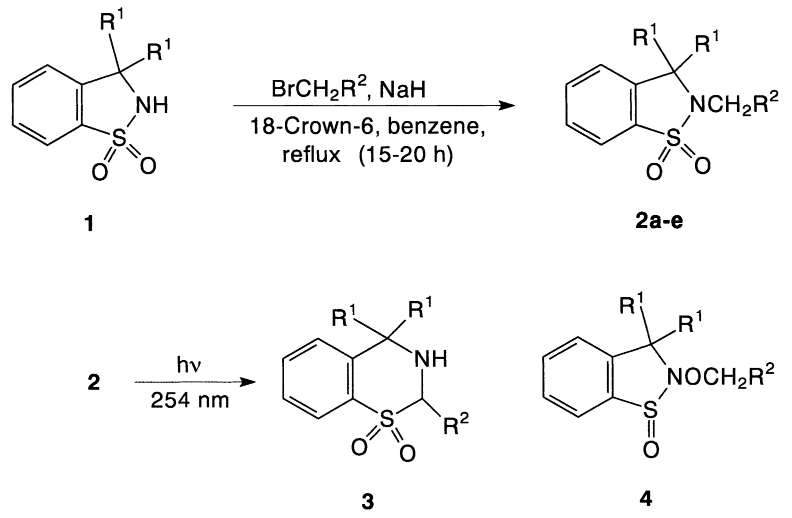
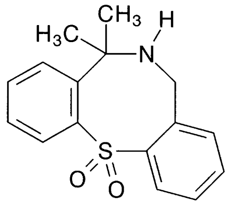


Scheme 1.

2a led to the formal oxygen shift[3–5] photoproduct **4a** besides **3a** (Scheme 1). The a priori alternative structure **5** could be ruled out on the basis of the spectral data[11] obtained for **4a**.



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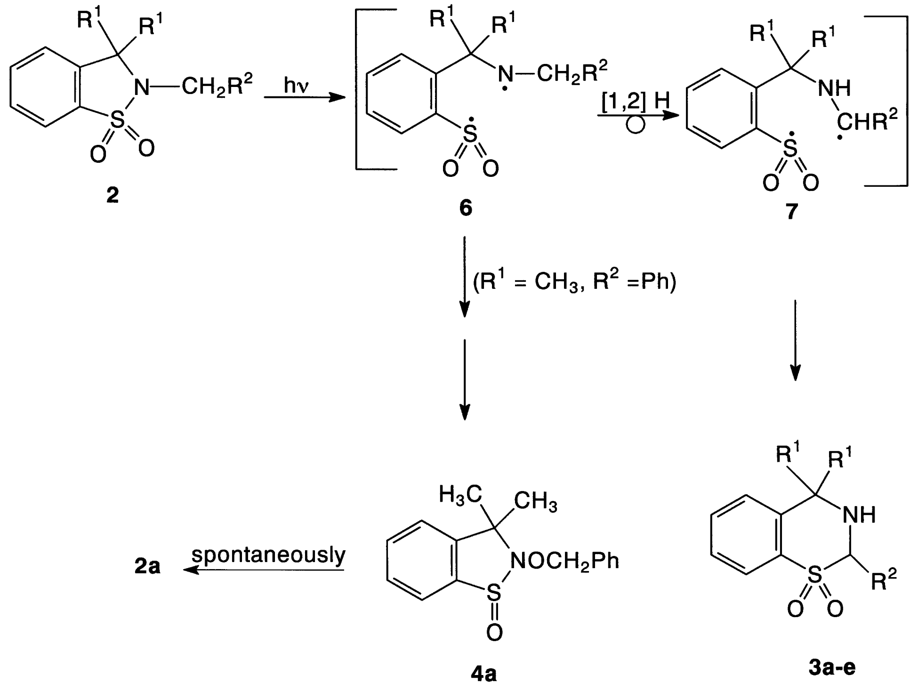
Furthermore, it has been reported[3,4] earlier that compounds having structure **4** could revert back to starting material upon standing at room temperature in protic solvents or exposure to acid. Therefore, it is not surprising that, while compound **4a** could be isolated (as an oil), after a short irradiation time (2 h) no **4a** was detected in the photolysis mixture after 6 h. When a sample of neat **4a** had been left standing for 2 weeks at room temperature, the flask only contained crystalline **2a**.

A rationale which explains the photoisomerization of **2** to **3** is outlined in Scheme 2.

Photoexcited **2** undergoes S–N bond homolysis[3–9] to give biradical **6**. A subsequent 1,2-hydrogen shift from carbon to nitrogen produces biradical **7** followed by cyclization to afford the final ring-expansion photo-



Scheme 2.

product **3**. It should be emphasized that the rearranged biradical **7** profits from benzylic ($R^2 = Ph$) or captodative[12] ($R^2 = CO_2Me$, CN, COMe) stabilization and hence there is a driving force for its formation. The photorearrangement of **3a** to the sulfine hydroxamic acid derivative **4a** has been discussed earlier[3–5] in other cases.

The assignment of the photo-ring-expansion products **3** was based on $^1H/^{13}C$ NMR spectra as well as on the mass spectra.[13] Thus, in the ^1H NMR spectra of compounds **3** the one-proton singlet was observed at d 5.27–5.85 ppm assigned to H-2, and the ^{13}C NMR spectra revealed signals at d 62.0–74.1 ppm assigned to the asymmetric carbon atoms C-2. Furthermore, in the mass spectrum of **3a** the major fragment at $m/z = 104$ is the equivalent of $C_6H_5CNH^+$. The 2-substituted 1,3-benzothiazines tend to lose a nitrile fragment as a characteristic fragment in the mass spectra.[14]

It is worth mentioning that all the UV spectra of the sultams **2a**–**e** typically showing structured absorptions in the 270–250 nm range with log ε values below 3 are dominated mainly by the benzoid ring as a chromophore.

In summary, a new and efficient one-step photoconversion of 2,3-dihydro-1,3-benzisothiazoles 1,1-dioxides to 1,3-benzothiazine 1,1-dioxides has been described. The yield of the reaction coupled with the easy conversion starting from readily available precursors makes this method a most expeditious and efficient one among the previously reported methods[14–16] for constructing similar ring systems.

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References

1. See for example: Lablache-Combier, A. In *Organic Photochemistry and Photobiology*; Horspool, W. M.; Song, P. S., Eds.; CRC Press: Boca Raton, FL, 1995; pp. (a) 803–823; (b) 1063–1120 and references cited therein.
2. Pavlik, J. W. In *Molecular and Supramolecular Photochemistry Volume 1 (Organic Photochemistry)*; Ramamurthy, V.; Schanze, K., Eds. The photochemistry of pyrazoles and isothiazoles. Marcel Dekker: New York, 1997; pp. 57–110 and references cited therein.
3. Döpp, D.; Krüger, C.; Lauterfeld, P.; Raabe, E. *Angew. Chem.* **1987**, *99*, 142–143; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 146–147.
4. Döpp, D.; Lauterfeld, P.; Schneider, M.; Schneider, D.; Seidel, U. *Phosphorus Sulfur Silicon Relat. Elem.* **1994**, *95–96*, 481–482.
5. Döpp, D.; Lauterfeld, P.; Schneider, M.; Schneider, D.; Henkel, G.; Issac, Y.; Elghamry, I. *Synthesis* **2001**, 1223–1227.
6. Elghamry, I.; Döpp, D.; Henkel, G. *Synthesis* **2001**, 1228–1235.
7. Kamigata, N.; Iizuka, H.; Kobayashi, M. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1601–1602.
8. (a) Sindler-Kulyk, M.; Neckers, D. C. *Tetrahedron Lett.* **1981**, *22*, 525–528; (b) Hoffman R. W.; Sieber, W.; Guhn, G. *Chem. Ber.* **1965**, *98*, 3470–3478.
9. (a) Kamigata, N.; Hashimoto, S.; Kobayashi, M.; Nakanishi, H.; *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3131–3136; (b) Kamigata, N.; Hashimoto, S.; Fujie, S.; Kobayashi, M. *J. Chem. Soc. Chem. Commun.* **1983**, 765–766.
10. Samples of sultams **2** (0.87 mmol) in methanol (or acetonitrile) (100 ml) were irradiated for the periods listed using a quartz immersion well in connection with a Hanau TNN 15 low-pressure mercury lamp (15 W input) with continuous argon purging. After concentration the residue was chromatographed on silica-gel layers (1 mm) using ethylacetate/*n*-hexane (1:1). R_f values refer to analytical TLC.
11. 2-Benzyloxy-2,3-dihydro-3,3-dimethyl-1,2-benzisothiazole 1-oxide (**4a**): $R_f = 0.13$ colorless viscous liquid; IR (KBr) ν 1144 (SO); ^1H NMR (300 MHz, $CDCl_3$) δ 1.59 (s, 3H, CH_3), 1.67 (s, 3H, CH_3), AB ($\delta_A = 4.18$, $\delta_B = 4.24$, $|J_{AB}| = 18$ Hz, CH_2), 7.48 (m, 9H, aryl-H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1 (CH_3), 23.1 (CH_3), 68.2 (C-4), 75.7 (CH_2), 117.6, 126.6, 128.1, 128.4, 129.2, 130.3, 132.1, 138.4, 142.6, 143.8; MS (70 eV) m/z (%) 287 (M^+, 3), 272 (28), 166 (4), 149 (11), 91 (100). Anal. calcd for $C_{16}H_{17}NO_2S$ (287.4): C, 66.87; H, 5.96; N, 4.87; S, 11.16. Found: C, 66.78; H, 6.01; N, 4.82; S, 11.11%. Compound **3a**: C, 66.71; H, 5.82; N, 4.63; S, 10.91%.
12. (a) Viele, H. G.; Janousek, Z.; Merényi, R.; Stella, L. *Acc. Chem. Res.* **1985**, *18*, 148–154; (b) Sustmann, R.; Korth, H.-G. *Adv. Phys. Org. Chem.* **1990**, *26*, 131–178.
13. 3,4-Dihydro-4,4-dimethyl-2-phenyl-1,3-2*H*-benzothiazine 1,1-dioxide (**3a**): $R_f = 0.23$ colorless crystals (from benzene); mp 207–208°C; IR (KBr) ν 3330 (broad, NH), 1279, 1141 (SO_2); ^1H NMR (500 MHz, $CDCl_3$) δ 1.56 (s, 3H, CH_3), 1.76 (s, 3H, CH_3), 3.17 (broad, 1H, NH), 5.50 (s, 1H, 2-H), 7.46 (m, 8H, aryl-H), 8.10 (d, 1H, aryl-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.4 (CH_3), 31.9 (CH_3), 55.1 (C-4), 72.6 (C-2), 124.6, 126.9, 127.6, 128.4, 128.8, 129.7, 132.3, 137.5, 145.7; MS (70 eV) m/z (%) 287 (M^+, 3), 272 (6), 208 (52), 168 (27), 104 (100), 91 (45), 76 (35).
14. Sindler-Kulyk, S.; Neckers, D. C. *J. Org. Chem.* **1983**, *48*, 1275–1281.
15. Zinnes, H.; Comes, R. A.; Shavel, J. *J. Org. Chem.* **1964**, *29*, 2068–2070.
16. Rothe, M.; Steinberger, R. *Tetrahedron Lett.* **1970**, 2467–2470.