PHOTOCHEMICAL TRANSFORMATION OF 2-NAPHTHYL-1,2-BENZISOTHIAZOLINONES

Nobumasa Kamigata,* Hirokazu Iizuka, and Michio Kobayashi
Department of Chemistry, Tokyo Metropolitan University
Fukazawa, Setagaya-ku, Tokyo 158, Japan

Abstract — Photochemical reaction of 2-naphthyl-1,2-benzisothiazol-3(2H)-ones in benzene under argon gives ring-expansion isomer, benzonaphthothiazepinone, probably via homolytic cleavage of the S-N bond and intramolecular recombination of the biradical, followed by the hydrogen shift to regeneration of an aromatic ring.

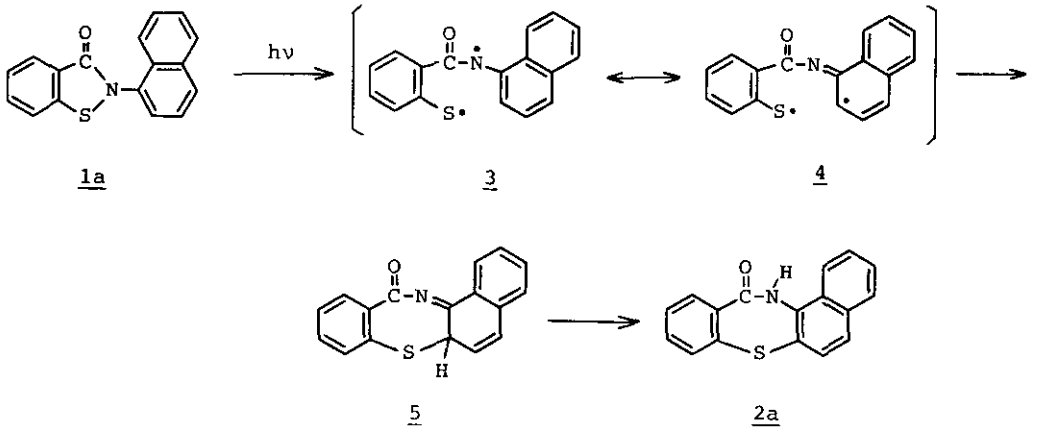
Recently, much attention has been focused on the photochemistry of five-membered heterocyclic system.[1] Previously, we reported that the photochemical reaction of 2-substituted 1,2-benzisothiazol-3(2H)-one 1,1-dioxides in benzene gave rise to N-substituted o-phenylbenzamides with the extrusion of sulfur dioxide,[2] whereas, the photolysis of 2-(4-substituted phenyl)-1,2-benzisothiazol-3(2H)-ones, which correspond to reduced derivatives of 2-substituted 1,2-benzisothiazol-3(2H)-one 1,1-dioxides, in benzene gave dibenzothiazepinones.[3] We describe here the photochemical reactions of 2-naphthyl-1,2-benzisothiazolinones (1).

When a solution containing 200 mg of 2-(1-naphthyl)-1,2-benzisothiazol-3(2H)-one[4] (1a) in 230 ml of benzene was irradiated under argon with a 450-W medium pressure mercury lamp (Hanovia) through a Pyrex filter for 1.5 h, a single photoproduct was obtained. An assignment of this material as benzo[f]naphtho[2,1-b][1,4]thiazepin-12(13H)-one (2a) was made on the basis of its spectral data.[5] It is of quite interest that a medium-size seven-membered ring compound was formed by a photochemical isomerization from five-membered heterocyclic compound 1a.

A reaction mechanism which explains the phototransformation is outlined in Scheme 1. The photoexcited 1a undergoes homolytic cleavage of the S-N bond to give biradical (3). The biradical recombinates at β-position of the N-naphthyl group to give the cyclized product (5). A subsequent hydrogen shift of intermediate 5

leads to the final product.[6]

It is known that thiyl radical does not attack an aromatic nucleus. However, in the present case high odd electron density at the β-position of the naphthalene ring is expected to be more reactive due to the resonance between 3 and 4, thus makes the recombination of the biradical 3 to give 5 quite feasible.



1a 3 4

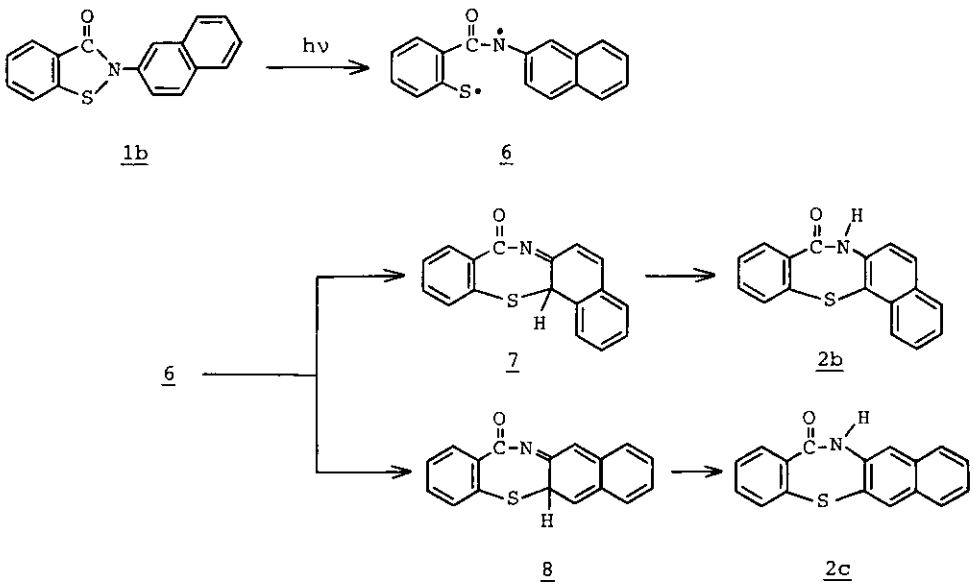
5 2a

Sheme 1

If this proposed mechanism is adequate, it is expected that the photochemical reaction of 2-(2-naphthyl)-1,2-benzisothiazol-3(2H)-one[4] (1b) will afford two photoisomerized products. As expected, two kind of photoproducts were isolated when 1b was irradiated in a similar manner in benzene. They were assigned as benzo[f]naphtho[1,2-b][1,4]thiazepin-8(7H)-one[7] (2b) and benzo[f]naphtho[2,3-b]thiazepin-13(12H)-one[8] (2c) on the basis of their spectral data.

The reaction path way of 1b will be similar to that of 1a. The biradical intermediate (6) would be formed by the irradiation of 1b, and the thiyl radical attacks the α- and β-position of intramolecular naphthalene nucleus giving the final product 2b and 2c, via cyclized products 7 and 8, respectively (Scheme 2). The product ratio of 2b and 2c was 2:1 which means that the thiyl radical 6 attacks the α-position of naphthalene ring two times faster than the β-position. It is well known that the α-position reacts ten times faster than the β-position in the intermolecular arylation of naphthalene by phenyl radical.[9] Selectivity in the present reaction is lower than the intermolecular phenylation. This may be attributed by the intramolecular nature of the recombination between biradical

center in the intermediate 6.



Scheme 2

REFERENCES

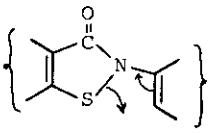
1. A. Padwa, "Rearrangement in Ground and Excited State," ed by P. de Mayo, Academic Press, New York, Vol. 3 (1980), p. 501; A. Lablache-Combier, "Photochemistry of Heterocyclic Compounds," ed by O. Buchardt, Wiley, New York (1976), p. 123.
2. N. Kamigata, T. Saegusa, S. Fujie, and M. Kobayashi, Chem. Lett., 1979, 9.
3. N. Kamigata, S. Hashimoto, S. Fujie, and M. Kobayashi, J. Chem. Soc., Chem. Commun., 1983, 765; N. Kamigata, S. Hashimoto, M. Kobayashi, and H. Nakanishi, Bull. Chem. Soc. Jpn., 58, 3131 (1985).
4. 2-(1-Naphthyl)- and 2-(2-naphthyl)-1,2-benzisothiazol-3(2H)-ones (1) were prepared from 2,2'-dithiobis[benzoyl chloride] by treating with 1-naphthylamine and 2-naphthylamine, respectively, according to the modified method of Reissert and Manns reported from our laboratory [N. Kamigata, S. Hashimoto, and M. Kobayashi, Org. Prep. Proc. Int., 15, 315 (1983)]. The yields of 1a and 1b were 89% and 65%, respectively, and the physical and spectral data are as follows:

1a: mp 128-130 °C; IR (KBr) 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 7.50-8.19 (11H, m); MS, m/z 277 (M^+); HRMS, m/z 277.0539 ($C_{17}H_{11}NOS$ requires 277.0561); UV (methanol) 320 (log ε = 4.35) and 285 nm (4.45).

1b: mp 166-167 °C; IR (KBr) 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 7.44-8.15 (11H, m); MS, m/z 277 (M^+); HRMS, m/z 277.0475 ($C_{17}H_{11}NOS$ requires 277.0561); UV (methanol) 335 (log ε = 3.93) and 255 nm (4.45).

5. 2a: Yield 29%; mp 270 °C; IR (KBr) 3000 (amide N-H) and 1635 cm^{-1} (amide C=O); ^1H NMR (methanol-d_4) 400 MHz δ = 7.403 (1H, t, J = 8 Hz), 7.442 (1H, t, J = 8 Hz), 7.650 (2H, d, J = 8 Hz), 7.628 (2H, d, J = 8 Hz), 7.734 (2H, t, J = 8 Hz), 7.782 (1H, d, J = 8 Hz), 8.150 (1H, d, J = 8 Hz), and 10.96 (1H, s); MS, m/z 277 (M^+); HRMS, m/z 277.0471 ($C_{17}H_{11}NOS$ requires 277.0561).

6. A mechanism involving orbital symmetry allowed concerted 1,3-rearrangement shown below can not be ruled out at present.



7. 2b: Yield 34%; mp 250 °C; IR (KBr) 3000 (amide N-H) and 1650 cm^{-1} (amide C=O); ^1H NMR (methanol-d_4) 400 MHz δ = 7.417 (1H, d, J = 8 Hz), 7.469 (1H, t, J = 8 Hz), 7.472 (1H, t, J = 8 Hz), 7.542 (1H, t, J = 8 Hz), 7.66-7.72 (3H, m), 7.929 (2H, d, J = 8 Hz), 8.659 (1H, d, J = 8 Hz), and 10.95 (1H, s); MS, m/z 277 (M^+); HRMS, m/z 277.0471 ($C_{17}H_{11}NOS$ requires 277.0561).

8. 2c: Yield 17%; mp 250 °C; IR (KBr) 3000 (amide N-H) and 1650 cm^{-1} (amide C=O); ^1H NMR (methanol-d_4) 400 MHz δ = 7.26 (1H, s), 7.37 (1H, s), 7.43 (2H, t, J = 8 Hz), 7.48 (1H, t, J = 8 Hz), 7.59 (1H, d, J = 8 Hz), 7.66 (1H, d, J = 8 Hz), 7.78 (1H, d, J = 8 Hz), 7.80 (1H, d, J = 8 Hz), 7.83 (1H, t, J = 8 Hz), 8.43 (1H, s), and 8.96 (1H, s); MS, m/z 277 (M^+); HRMS, m/z 277.0577 ($C_{17}H_{11}NOS$ requires 277.0561).

9. D. I. Davies, D. H. Hey, and G. H. Williams, J. Chem. Soc., 1961, 3112.

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