Photochemical Isomerization of 2-Pyridyl- and 2-Pyrazinyl-1,2-benzisothiazol-3(2*H*)-ones

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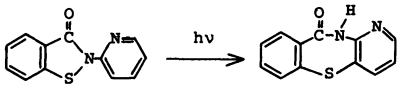
Synopsis. The irradiation of 2-pyridyl- and 2-pyrazinyl-1,2-benzisothiazol-3(2*H*)-ones in benzene resulted in the formation of benzopyrido- and benzopyrazinothiazepinones, respectively. A mechanism involving a biradical species is proposed for this reaction.

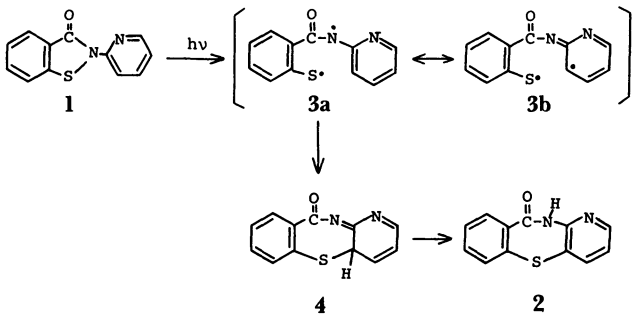
Considerable attention has been focused in recent years on the photochemistry of five-membered heterocyclic ring systems. By far the greatest area of activity in this field has been a study of the photoisomerization that results in a change in the heterocyclic nucleus.[1] We have reported a novel photochemical ring-expansion reaction of such five-membered heterocyclic compound as 2-aryl-1,2-benzisothiazolinones to seven-membered heterocyclic compound, dibenzothiazepinones.[2] As we have continuous interest in this novel photoisomerization, the photochemical reaction of 2-pyridyl- and 2-pyrazinyl-1,2-benzisothiazol-3(2*H*)-ones has been studied and the results are described herein.

When a solution containing 2-(2-pyridyl)-1,2-benzisothiazol-3(2*H*)-one (**1**) in benzene was irradiated under argon with 300-nm light, a single photoproduct was obtained. This material was assigned as benzo[*f*]pyrido[3,2-*b*][1,4]thiazepin-10(11*H*)-one (**2**) on the basis of its spectral data.



1 **2**

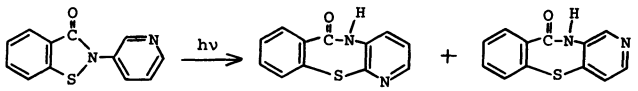
This reaction is of interest since it involves a medium-size seven-membered ring compound, is generally difficult to prepare and is obtained by photochemical isomerization from a five-membered compound involving a pyridine ring **1**. The photoreaction is presumed to proceeded via a homolytic cleavage of the S–N bond to generate a biradical **3**. The initially-formed thiyl radical of **3a** attacks the β-position of the *N*-(2-pyridyl) group to give a cyclized product **4**. A subsequent 1,7-hydrogen shift of the intermediate **4** leads to the final product **2** (Scheme 1).



1 **3a** **3b** **4** **2**

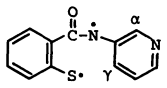
Scheme 1.

For this proposed mechanism to be adequate, it was expected that a photochemical reaction of 2-(3-pyridyl)-1,2-benzisothiazol-3(2*H*)-one (**5**) would afford two photoisomerized products. As expected, the irradiation of **5** in benzene in a similar way afforded two isomeric photoreaction products. They were assigned as benzo[*f*]pyrido[2,3-*b*][1,4]thiazepin-6(5*H*)-one (**6**) and benzo[*f*]pyrido[4,3-*b*][1,4]thiazepin-10(11*H*)-one (**7**) on the basis of their spectral data.



5 **6** **7**

The fact that almost equal amounts of photoisomeric products (**6** and **7**) were obtained in the photolysis of **5** suggests that the selectivity of the thiyl radical of the intermediate **8**, formed from **5** by the photochemical cleavage of the S–N bond, is extremely weak regarding on intramolecular attack on α- and γ-positions of the pyridine ring.



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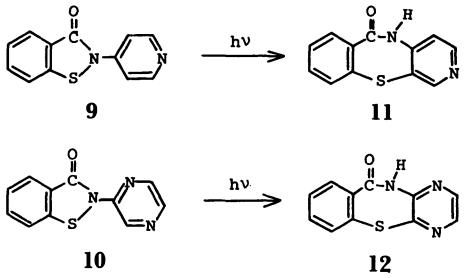
The photochemical reactions of 2-(4-pyridyl)-1,2-benzisothiazol-3(2*H*)-one (**9**) and 2-(2-pyrazinyl)-1,2-benzisothiazol-3(2*H*)-one (**10**) were also studied. In these cases, a single photoproduct, benzo[*f*]pyrido-[3,4-*b*][1,4]thiazepin-6(5*H*)-one (**11**) and benzo[*f*]-pyrazino[2,3-*b*][1,4]thiazepin-10(11*H*)-one (**12**) were isolated, respectively, for each reaction.



9 **11** **10** **12**

Experimental

All melting points were uncorrected. IR and UV spectra were recorded on a Hitachi EPI-G2 and a Hitachi 220A spectrometer. ^{1}H NMR spectra were measured with a

Hitachi R-90H (90 MHz) spectrometer using tetramethylsilane as an internal standard. Mass spectra were determined with a JEOL JMS-DX300 high-resolution mass spectrometer with a JEOL JMA5000 mass-data system at an ionization energy of 70 eV.

Materials. 2-Pyridyl- and 2-pyrazinyl-1,2-benzisothiazol-3(2*H*)-ones were prepared from 2,2′-dithiobis[benzoyl chloride] by treating with aminopyridine and aminopyrazine, respectively, according to a modified method of Reissert and Manns.[3] The yields, physical properties, and spectral data were as follows:

2-(2-Pyridyl)-1,2-benzisothiazol-3(2*H*)-one (1): Yield 84%; mp 194.5—195.5 °C (from $CHCl_3$); IR (KBr) 1675 cm^{-1}; ^1H NMR (DMSO-d_6) δ=7.07—7.90 (5H, m), 8.07 (1H, d, J=7.7 Hz), 8.41 (1H, d, J=5.1 Hz), and 8.75 (1H, d, J=8.4 Hz); ^{13}C NMR ($CDCl_3$) δ=114.39, 120.24, 120.61, 125.43, 126.57, 126.73, 132.74, 138.30, 140.98, 147.51, 150.36, and 163.95; MS, m/z 228 (M^+); HRMS, m/z 228.0419 ($C_{12}H_8N_2OS$ requires 228.0357); UV (methanol) 255 (log ε=3.98) and 335 nm (3.81).

2-(3-Pyridyl)-1,2-benzisothiazol-3(2*H*)-one (5): Yield 78%; mp 118.5—119.5 °C (from $CH_3CO_2C_2H_5$); IR (KBr) 1675 cm^{-1}; ^1H NMR (DMSO-d_6) δ=7.26—7.73 (4H, m), 8.11 (1H, dd, J=7.6 and 1.0 Hz), 8.15—8.27 (1H, m), 8.55 (1H, dd, J=4.7 and 1.3 Hz), and 8.95 (1H, d, J=2.4 Hz); ^{13}C NMR (DMSO-d_6) δ=120.18, 123.69, 124.01, 126.03, 127.13, 132.72, 134.41, 134.41, 139.60, 144.86, 147.46, and 164.27; MS, m/z 228 (M^+); HRMS, m/z 228.0339 ($C_{12}H_8N_2OS$ requires 228.0357); UV (methanol) 254 (log ε=4.11) and 330 nm (3.73).

2-(4-Pyridyl)-1,2-benzisothiazol-3(2*H*)-one (9): Yield 88%; mp 182.5—183.5 °C (from CH_3OH); IR (KBr) 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.43—8.14 (6H, m), 8.66 (2H, dd, J=4.3 and 1.2 Hz); ^{13}C NMR ($CDCl_3$) δ=115.84, 122.20, 126.16, 126.16, 126.49, 133.63, 139.60, 144.21, 146.16, 149.08, and 164.21; MS, m/z 228 (M^+); HRMS, m/z 228.0339 ($C_{12}H_8N_2OS$ requires 228.0357).

2-(2-Pyrazinyl)-1,2-benzisothiazol-3(2*H*)-one (10): Yield 87%; mp 152—153 °C (from CH_3OH); IR (KBr) 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.36—7.70 (3H, m), 8.08 (1H, d, J=7.9 Hz), 8.40 (1H, d, J=7.9 Hz), 8.42 (1H, s), and 10.03 (1H, s); MS, m/z 229 (M^+); HRMS, m/z 229.0294 ($C_{11}H_7N_3OS$ requires 229.0294); UV (methanol) 235 (log ε=3.60) and 345 nm (4.27).

Photolysis of 2-Pyridyl- or 2-Pyrazinyl-1,2-benzisothiazol-3(2*H*)-one. A solution containing 200 mg of **1**, **5**, **9**, or **10** in 230 cm^3 of benzene was irradiated using a 450-W Hanovia medium-pressure mercury lamp through a Pyrex filter sleeve for 40 h. The removal of the solvent under reduced pressure left a light-brown residue which was purified by silica-gel chromatography using dichloromethane–ethyl acetate 4:1 mixture as the eluent. The yield and physical and spectral data of these photoreaction products are as follows:

Benzo[*f*]pyrido[3,2-*b*][1,4]thiazepin-10(11*H*)-one (2): Yield 59%; mp 239—240 °C; IR (KBr) 2900—3200 (w, amide N–H) and 1650 cm^{-1} (s, amide C=O); ^1H NMR (DMSO-d_6) δ=7.20 (1H, dd, J=7.7 and 4.7 Hz), 7.46—7.75 (4H, m), 8.01 (1H, dd, J=7.7 and 1.8 Hz), 8.38 (1H, dd, J=4.7 and 1.8 Hz), and 10.98 (1H, s); MS, m/z 228 (M^+); HRMS, m/z 228.0465 ($C_{12}H_8N_2OS$ requires 228.0357).

Benzo[*f*]pyrido[2,3-*b*][1,4]thiazepin-6(5*H*)-one (6): Yield 23%; mp 300 °C; IR (KBr) 2900—3200 (w, amide N–H) and 1660 cm^{-1} (s, amide C=O); ^1H NMR (DMSO-d_6) δ=7.38—7.72 (6H, m), 8.28 (1H, dd, J=4.4 and 1.8 Hz), and 10.68 (1H, s); MS, m/z 228 (M^+); HRMS, m/z 228.0438 ($C_{12}H_8N_2OS$ requires 228.0357).

Benzo[*f*]pyrido[4,3-*b*][1,4]thiazepin-10(11*H*)-one (7): Yield 21%; mp 240—241 °C; IR (KBr) 2900—3200 (w, amide N–H) and 1660 cm^{-1} (s, amide C=O); ^1H NMR (DMSO-d_6) δ=7.40—7.77 (5H, m), 8.30 (1H, d, J=5.1 Hz), 8.43 (1H, s), and 10.82 (1H, s); MS, m/z 228 (M^+); HRMS, m/z 228.0384 ($C_{12}H_8N_2OS$ requires 228.0357).

Benzo[*f*]pyrido[3,4-*b*][1,4]thiazepin-6(5*H*)-one (11): Yield 40%; mp 244 °C; IR (KBr) 3170 (w, amide N–H) and 1660 cm^{-1} (s, amide C=O); ^1H NMR (DMSO-d_6) δ=7.20 (1H, d, J=5.3 Hz), 7.42—7.77 (4H, m), 8.42 (1H, d, J=5.3 Hz), 8.63 (1H, s), and 11.03 (1H, s); MS, m/z 228 (M^+); HRMS, m/z 228.0438 ($C_{12}H_8N_2OS$ requires 228.0357).

Benzo[*f*]pyrazino[2,3-*b*][1,4]thiazepin-10(11*H*)-one (12): Yield 45%; mp 232—233 °C; IR (KBr) 3100 (w, amide N–H) and 1650 cm^{-1} (s, amide C=O); ^1H NMR ($CDCl_3$) δ=7.40—7.47 (4H, m), 8.30 (2H, s), and 13.77 (1H, s); MS, m/z 229 (M^+); HRMS, m/z 229.0255 ($C_{11}H_7N_3OS$ requires 229.0305).

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References

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