Photochemical Ring-expansion Reaction of 1,2-Benzisothiazolinones

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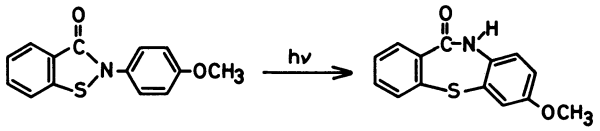
The photochemical reaction of a series of 2-aryl-1,2-benzisothiazol-3(2*H*)-ones (**1**) under deaerated conditions was found to give dibenzo[*b*,*f*][1,4]thiazepin-11(10*H*)-ones (**2**). A mechanism through a biradical species is proposed for the photoreaction. When the photolysis of **1** was carried out in the presence of oxygen, 2-aryl-1,2-benzisothiazol-3(2*H*)-one 1-oxides (**11**) were formed together with compounds **2**.

In recent years much attention has been focused on the photochemistry of five-membered heterocyclic ring systems. These studies have dealt with the synthetic usefulness of the photochemistry of heterocyclic compounds as well as their reaction modes.[1-4] In earlier communications we reported that the photochemical reaction of 2-substituted 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxides in benzene gave rise to *N*-substituted *o*-phenylbenzamides with the extrusion of sulfur dioxide,[5] whereas, the photolysis of 2-aryl-1,2-benzisothiazol-3(2*H*)-one, which corresponds to reduced derivatives of *N*-substituted 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxides in benzene, gave dibenzothiazepinones.[6] We give here a full account for the photochemical behavior of a series of 2-aryl-1,2-benzisothiazol-3(2*H*)-ones (**1**).

Results and Discussion

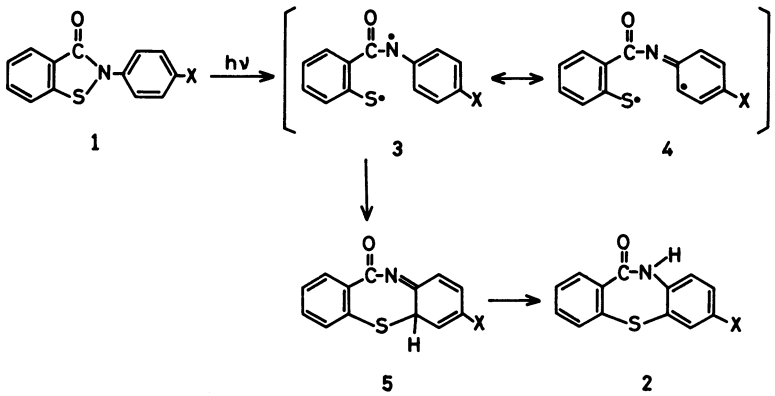
When a deaerated solution of 2-(4-methoxyphenyl)-1,2-benzisothiazol-3(2*H*)-one (**1a**) in benzene was irradiated with 340-nm wavelength light, a single photoproduct was obtained. An assignment of this material as 7-methoxydibenzo[*b*,*f*][1,4]thiazepin-11-(10*H*)-one (**2a**) was made on the basis of its spectral data, especially its 400-MHz ^{1}H NMR spectrum.



1a **2a**

Several related 2-aryl-1,2-benzisothiazol-3(2*H*)-ones (**1**) were also irradiated under similar conditions to give dibenzo[*b*,*f*][1,4]thiazepin-11(10*H*)-ones (**2**) as the only isolable photoproducts. The results are summarized in Table 1. A reaction mechanism which explains the phototransformation is outlined in Scheme 1. The photoexcited **1** undergoes homolytic cleavage of the weakest bond (S–N) in the molecule to give biradical (**3**). The initially-formed biradical attacks the ortho-position of the *N*-aryl group to give the cyclized product **5**. A subsequent 1,7-hydrogen shift of intermediate **5** leads to the final product. The last step of the sequence can proceed by either a thermal or photochemical hydrogen shift.

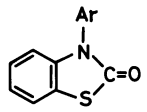
Recently, Rokach and Hammel reported that a small amount of a photo-ring expansion product was formed together with 3-phenylthiazol-2(3*H*)-one upon irradiation of 2-phenylisothiazol-3(2*H*)-one.[7] However, we could not detect the corresponding 3-aryl-2(3*H*)-benzothiazolone (**6**) in the reaction mixture.



1 **3** **4** **5** **2**

Scheme 1.

According to the mechanism proposed,[7] a ring-contracted intermediate such as **7** would seem reasonable. The absence of compound **6** among the products suggests that this intermediate (*i.e.* **7**) is not formed in the photoreaction of **1**. The absence of **7**



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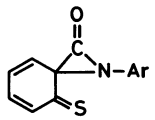

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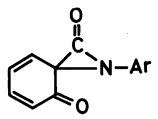
can be accounted for in terms of the high energy required to interrupt the aromaticity of the benzene ring. The photo-transposition reaction of the related 2-alkyl-1,2-benzisoxazol-3(2*H*)-one system to 3-alkyl-1,2-benzoxazol-2(3*H*)-one *via* the ring-contracted intermediate **8** was reported by Kinstle and co-workers.[8] Therefore, the absence of **7** can be also attributed to the instability of the C=S group ($2p\pi$—$3p\pi$) compared with the C=O group ($2p\pi$—$2p\pi$).



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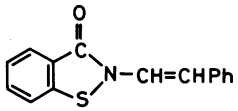
Recently, Kulyk and Neckers have reported the intermolecular photoaddition of the benzisothiazole system to alkenes and alkynes and demonstrated the synthetic usefulness of benzothiazepines.[9] Our present reaction is of interest from both mechanistic and synthetic points of view since medium-size seven-membered ring compounds are generally very difficult to prepare. Unfortunately, the yield of **2** is low as is shown in Table 1. This can be attributed to the fact that biradical **3** gives rise to polymeric compounds at a faster rate than an intramolecular reaction to give **2**. If this postulate is correct, the yield of **2** would be expected to improve with the use of a more viscous solvent. The irradiation of **1b** was carried out in *t*-butyl alcohol using a Tungsten filter. However, no difference in the yield of **2b** was observed. Then, **1b** was irradiated in *t*-butyl alcohol using a Pyrex, Corex or Vycor filter to determine whether the wavelength of light would affect the yield of **2**. A considerable improvement was observed with the latter two filters. When compound **1b** was irradiated through a Corex filter in either *t*-butyl alcohol, benzene or methanol, the yield of **2b** was low in the latter two solvents. The results are summarized in Table 2. These results imply that both the wavelength of the light and the solvent are important in the photoreaction of compound **1** to obtain the photoproduct **2** in a good yield. Since the yield of compound **2b** was improved upon irradiation through a Corex filter in *t*-butyl alcohol, several related compounds were irradiated under similar conditions (Table 3). We found that an improvement in the yield occurred only when the *N*-phenyl group of **1** possesses an electron-donating substituent.

We also studied the photoreaction of (*E*)-2-styryl-1,2-benzisothiazol-3(2*H*)-one (**9**) expecting the formation of a photoexpansion product (**10**). However,



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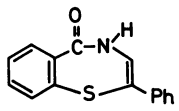

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Table 1. Photochemical reaction of **1** in benzene[a]

X in **1**		Product	Yield/%[b]
1a	OCH_3	**2a**	13
1b	CH_3	**2b**	19
1c	H	**2c**	16
1d	Cl	**2d**	17
1e	CN	**2e**	11

a) The irradiation was carried out on a 2×10^{-3} M solution of **1** in benzene under degassed conditions using a 450 W medium-pressure mercury lamp (Hanovia) through a Tungsten glass filter (>340 nm). In case of **1e**, a Molybdenum glass filter (>320 nm) was employed. b) The yields are based on the starting material consumed.

Table 2. Effect of wavelength and viscosity of solvent in the photolysis of **1b**

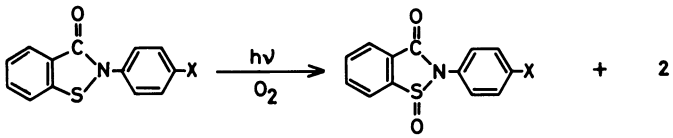
Solvent	Rel. Viscosity η (m Poise)	Filter		Yield of **2b**/%
Benzene	6.5 (20 °C)	Tungsten	340 nm	19
t-BuOH	33.2 (30 °C)	Tungsten	340 nm	14
t-BuOH		Pyrex	300 nm	18
t-BuOH		Corex	280 nm	57
t-BuOH		Vycor	250 nm	54
t-BuOH	33.2 (30 °C)	Corex	280 nm	57
Benzene	6.5 (20 °C)	Corex	280 nm	13
MeOH	5.5 (20 °C)	Corex	280 nm	7

Table 3. Photochemical reaction of **1** in *t*-butyl alcohol

X in **1**		Filter		Product	Yield/%
1a	OCH_3	Vycor	250 nm	**2a**	47
1b	CH_3	Corex	280 nm	**2b**	57
1c	H	Corex	280 nm	**2c**	31
1d	Cl	Vycor	250 nm	**2d**	13
1e	CN	Vycor	250 nm	**2e**	20

no photochemical transformation was observed upon irradiation for long periods of time (≈30 h) and all of the starting material **9** was recovered.

Irradiation of **1a** was also carried out in benzene using light of wavelength >340 nm in the presence of oxygen. Under these conditions, 2-(4-methoxyphenyl)-1,2-benzisothiazol-3(2*H*)-one 1-oxide (**11a**) was formed in 8% yield in addition to compound **2a**. The structure of **11a** was verified by a comparison with an authentic sample which was prepared by a treatment of **1a** with *N*-chlorosuccinimide, followed by a reaction with aqueous potassium hydrogencarbonate. Several related 2-aryl-1,2-benzisothiazol-3(2*H*)-ones **1** were also irradiated under similar conditions and were found to give the corresponding photo-oxidized product (**11**) together with compound **2**. The results are summarized in Table 4.



1 11

The mechanism of the photo-oxidation reaction is of considerable interest. We believe that compound **1** does not act as a sensitizer to form singlet oxygen since the triplet energy of **1** is estimated to be greater than 250 KJ per mol.[10] Therefore, the formation of singlet oxygen as the oxidant can be ruled out. Moreover, singlet oxygen is known not to oxidize diphenyl sulfide in benzene.[11] An alternate possibility involves the formation of an excited complex (**12**) resulting from the interaction of compound **1** and oxygen. Unfortunately, all attempts to detect such an intermediate by spectroscopic methods failed. Tezuka and co-workers have reported that a related complex, such as **13**, could indeed be detected spectroscopically in the photoreaction of diphenyl sulfide[12] with oxygen and they ruled out a mechanism which involves singlet oxygen as an intermediate.[13]

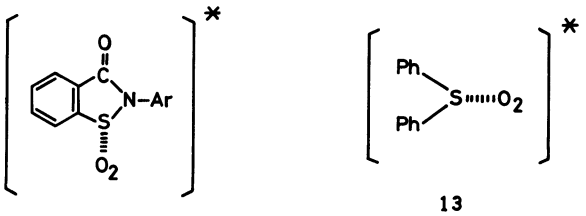


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Table 4. Photochemical reaction of **1** in the presence of oxygen[a]

X in **1**		Solvent	Product	Yield[b]		
1a	OCH_3	Benzene	**12a**	8%	**2a**	12%
1a	OCH_3	Methanol	**12a**	9%	**2a**	11%
1b	CH_3	Benzene	**12b**	9%	**2b**	16%
1c	H	Benzene	**12c**	8%	**2c**	15%
1c	H	Methanol	**12c**	10%	**2c**	15%
1d	Cl	Benzene	**12d**	11%	**2d**	14%
1e	CN	Benzene	**12e**	17%	**2e**	29%

a) Irradiation with a medium-pressure 450 W mercury lamp (Hanovia) through a Tungsten filter (>340 nm) under bubbling oxygen. In case of **1e**, a Molybdenum filter (>320 nm) was used. b) Yields (isolated) are based on the starting materials consumed.

Experimental

Measurement. Melting points are uncorrected. The infrared absorption spectra were determined on a Hitachi Model 260—10 spectrophotometer using KBr disks. The electronic spectra were determined on a Hitachi Model 220A spectrophotometer. The NMR spectra were recorded at 60 and 400 MHz using a Hitachi R20B and a JEOL JNM-GX400 spectrometer, respectively, with Me_4Si as an internal standard. Mass spectra were determined with a JEOL JMS-DX300 mass spectrometer with a JEOL JMA 5000 mass-data system at an ionizing voltage of 20—70 eV. Elemental analyses were carried out using a Perkin Elmer 240 elemental analyzer.

Preparation of 2-Aryl-1,2-benzisothiazol-3(2H)-ones (1). An improved method of Reissert and Manns[14] was employed for the syntheses of **1**. A solution containing 2,2′-dithiobis[benzoyl chloride] (2.0 g, 5.0 mmol) in dry dichloromethane (100 cm^3) was added dropwise at the ambient temperature to a well stirred solution of substituted aniline (29 mmol) in dry dichloromethane (50 cm^3) over a period of 15 min. The resulting mixture was stirred at room temperature for 3 h; then, the solvent was evaporated under reduced pressure. The residue was stirred with 1 M† hydrochloric acid (100 cm^3) for 30 min at room temperature to remove any excess aniline. The solid product, *N,N′*-diaryl-2,2′-dithiobis[benzamide], was collected, washed with water, and dried in a desiccator. A solution of bromine (1.4 g, 8.7 mmol) in dichloromethane was added dropwise at ambient temperature to a well stirred suspension of the *N,N′*-diaryl-2,2′-dithiobis[benzamide] (5.8 mmol) in dichloromethane (150 cm^3) over a period of 3—5 min. Stirring was continued at room temperature overnight. Activated basic alumina (Wako Pure Chemical, 300 mesh, 20 g) was added to the reaction mixture and stirring was continued for an additional 3 h. Removal of the solvent left a pale-yellow residue which was chromatographed over an activated alumina column (300 mesh, 40 g) and eluted with chloroform to give pure **1**. The following compounds were prepared using the above procedure.

2-(4-Methoxyphenyl)-1,2-benzisothiazol-3(2H)-one (1a): Yield, 96%; mp 148—149 °C (lit[15], mp 147—149 °C); ^1H NMR (Me_2SO-d_6) 400 MHz, δ=3.819 (3H, s, OCH_3), 7.085 and 7.569 (2H and 2H, A_2B_2 quartet, J_{AB}=8.9 Hz, 3′- and 2′-H), 7.509 (1H, m, J_{5-4}=8 Hz, J_{5-6}=7.0 Hz, 5-H), 7.764 (1H, m, J_{6-5}=7 Hz, J_{6-7}=8 Hz, 6-H), 7.951 (1H, d, J_{7-6}=8 Hz, 7-H),

† 1 M=1 mol dm^{-3}.

and 8.042 (1H, d, J_{4-5}=8 Hz, 4-H); ^{13}C NMR (Me_2SO-d_6) 400 MHz, δ=163.23 (C=O), 129.58 and 140.10 (3a- and 7a-C), 126.00, 125.80, 132.27, and 121.68 (4-, 5-, 6-, and 7-C), 124.10 (1′-C), 126.60 (2′-C), 114.55 (3′-C), 158.18 (4′-C), and 55.41 (OCH_3).

*2-(4-Methylphenyl)-1,2-benzisothiazol-3(2H)-one (**1b**)*: Yield 96%; mp 136—137 °C (lit,[16] mp 135.5—136.5 °C); ^{1}H NMR (Me_2SO-d_6) 400 MHz, δ=2.360 (3H, s, CH_3), 7.333 and 7.570 (2H and 2H, A_2B_2 quartet, J_{AB}=8.9 Hz, 3′- and 2′-H), 7.509 (1H, m, J_{5-4}=8 Hz, J_{5-6}=7 Hz, 5-H), 7.760 (1H, m, J_{6-5}=7 Hz, J_{6-7}=8 Hz, 6-H), 7.951 (1H, d, J_{7-6}=8 Hz, 7-H), and 8.051 (1H, d, J_{4-5}=8 Hz, 4-H); ^{13}C NMR (Me_2SO-d_6) 400 MHz, δ=163.20 (C=O), 129.73 and 139.98 (3a- and 7a-C), 126.02, 125.85, 132.37, and 121.70 (4-, 5-, 6-, and 7-C), 134.55 (1′-C), 129.73 (2′-C), 124.37 (3′-C), 136.49 (4′-C), and 20.51 (CH_3).

*2-Phenyl-1,2-benzisothiazol-3(2H)-one (**1c**)*: Yield 91%; mp 141.5—142.5 °C (lit,[14] mp 143—144 °C); ^{1}H NMR ($CDCl_3$) δ=7.2—8.3 (9H, m); ^{13}C NMR (Me_2SO-d_6) δ=164.3 (C=O), 128.2 and 145.4 (3a- and 7a-C), 125.1, 126.6, 133.3, and 134.5 (4-, 5-, 6-, and 7-C), 133.9 (1′-C), 127.2 (2′-C), 129.6 (3′-C), and 128.8 (4′-C).

*2-(4-Chlorophenyl)-1,2-benzisothiazol-3(2H)-one (**1d**)*: Yield 87%; mp 128—129 °C (lit,[15] mp 129—130 °C); ^{1}H NMR ($CDCl_3$) 400 MHz, δ=7.504 and 7.743 (2H and 2H, A_2B_2 quartet, J_{AB}=8.9 Hz, 3′- and 2′-H), 7.52 and 7.74 (1H and 1H, m, J_{5-4}=8 Hz, J_{5-6}=7 Hz, and J_{6-7}=8 Hz, J_{6-5}=7 Hz, 5- and 6-H), 7.657 (1H, d, J_{7-6}=8 Hz, 7-H), and 8.170 (1H, d, J_{4-5}=8 Hz, 4-H); ^{13}C NMR ($CDCl_3$) 400 MHz, δ=164.03 (C=O), 129.41 and 139.66 (3a- and 7a-C), 127.22, 125.92, 132.50, and 120.09 (4-, 5-, 6-, and 7-C), 135.91 (1′-C), 125.48 (2′-C), 129.41 (3′-C), and 124.64 (4′-C).

*2-(4-Cyanophenyl)-1,2-benzisothiazol-3(2H)-one (**1e**)*: Yield 95%; mp 184.5—185.5 °C, IR (KBr) 2220 (m, C≡N) and 1652 cm^{-1} (s, amide C=O); ^{1}H NMR ($CDCl_3$) 60 MHz, δ=7.86 and 8.08 (2H and 2H, A_2B_2 quartet, J_{AB}=9 Hz) and 7.4—8.3 (4H, m); ^{13}C NMR ($CDCl_3$) 60 MHz, δ=164.1 (C=O), 124.5 and 131.9 (3a- and 7a-C), 127.4, 126.2, 133.2, and 120.1 (4-, 5-, 6-, and 7-C), 141.6 (1′-C), 123.2 (2′-C), 133.2 (3′-C), 118.2 (4′-C), and 109.5 (C≡N); UV (methanol) 203 (ε=3.5×10^4), 239 (2.2×10^4), 279 (1.7×10^4), and 340 nm (7.8×10^3); MS, *m/z* 252 (M$^+$). Anal. Calcd for $C_{14}H_8N_2OS$: C, 66.65; H, 3.20; N, 11.10. Found: C, 66.72; H, 3.09; N, 11.15.

*Photolysis of 2-Aryl-1,2-benzisothiazol-3(2H)-one (**1**) in a Degassed Solution.* A solution containing 0.44 mmol of 2-aryl-1,2-benzisothiazol-3(2*H*)-one (**1**) in 220 cm^3 of benzene or *t*-butyl alcohol was degassed by a freeze-thaw method and irradiated through a filter sleeve using a 450-W Hanovia medium-pressure mercury lamp for 2 h. The removal of the solvent under reduced pressure left a light-brown residue which was purified by silica-gel chromatography using dichloromethane-hexane as the eluent. Photoproduct **2** was isolated with recovered starting material **1**. The physical and spectral data, and analyses of the photoproducts **2** are as follows:

*7-Methoxydibenzo[b,f][1,4]thiazepin-11(10H)-one (**2a**).* Mp 234—235 °C; IR (KBr) 1655 (aromatic amide C=O) and 2900—3300 cm^{-1} (m, complex N-H); ^{1}H NMR (Me_2SO-d_6) 400 MHz, δ=3.734 (3H, s, OCH_3), 6.947 (1H, dd, J_{8-9}=8.8 Hz, J_{8-6}=2.9 Hz, 8-H), 7.114 (1H, d, J_{6-8}=2.9 Hz, 6-H), 7.152 (1H, d, J_{9-8}=8.8 Hz, 9-H), 7.44 and 7.48 (1H and 1H, m, 2- and 3-H), 7.525 (1H, d, J_{4-3}=7.3 Hz, 4-H), 7.678 (1H, d, J_{1-2}=7.3 Hz, 1-H), and 10.153 (1H, s, *N*-H); ^{13}C NMR (Me_2SO-d_6) 400 MHz, δ=168.07 (C=O), 131.30, 131.12, 131.69, and 128.81 (1-, 2-, 3-, and 4-C), 137.75 and 136.13 (4a- and 11a-C), 130.39, 156.34, and 132.74 (5a-, 7-, and 9a-C), 156.34, 115.78, and 124.21 (6-, 8-, and 9-C), and 55.48 (OCH_3); UV (methanol) 206 (ε=3.7×10^3), 237 (1.5×10^4), and 285 nm (5.4×10^3); MS, *m/z* 257 (M$^+$). Anal. Calcd for $C_{14}H_{11}NO_2S$: C, 65.37; H, 4.31; N, 5.44. Found: C, 64.88; H, 4.36; N, 5.45.

*7-Methyldibenzo[b,f][1,4]thiazepin-11(10H)-one (**2b**).* Mp 274—275 °C; IR (KBr) 1660 (aromatic amide C=O) and 2900—3300 cm^{-1} (m, complex *N*-H); ^{1}H NMR (Me_2SO-d_6) 400 MHz, δ=2.240 (3H, s, CH_3), 7.119 (1H, d, J_{8-9}=8.1 Hz, 8-H), 7.158 (1H, d, J_{9-8}=8.1 Hz, 9-H), 7.377 (1H, broad s, 6-H), 7.43 and 7.47 (1H and 1H, m, J_{3-2}=J_{2-3}=7 Hz, J_{3-4}=J_{2-1}=7.3 Hz), 7.510 (1H, d, J_{4-3}=7.3 Hz, 4-H), and 7.671 (1H, s, *N*-H); ^{13}C NMR (Me_2SO-d_6) δ=168.20 (C=O), 131.17, 131.17, 131.71, and 128.70 (1-, 2-, 3-, and 4-C), 137.86 and 136.31 (4a- and 11a-C), 134.80, 134.80, and 137.26 (5a-, 7-, and 9a-C), 130.20, 122.93, and 132.53 (6-, 8-, and 9-C), and 19.86 (CH_3); UV (methanol) 208 (ε=4.2×10^4) and 280 nm (4.2×10^3); MS, *m/z* 241 (M$^+$). Anal. Calcd for $C_{14}H_{11}NOS$: C, 69.68; H, 4.59; N, 5.80. Found: C, 69.69; H, 4.65; N, 5.62.

*Dibenzo[b,f][1,4]thiazepin-11(10H)-one (**2c**).* Mp 264—265 °C; IR (KBr) 1645 (s, aromatic amide C=O) and 2900—3200 cm^{-1} (m, complex *N*-H); ^{1}H NMR (Me_2SO-d_6) δ=7.0—8.0 (m, aromatic-H); ^{13}C NMR (Me_2SO-d_6)δ=169.1 (C=O), 132.8, 132.1, 133.3, and 130.6 (1-, 2-, 3-, and 4-C), 140.6 and 137.1 (4a- and 11a-C), 133.3, 126.1, and 138.6 (5a-, 7-, and 9a-C), and 129.7, 132.1, and 123.9 (6-, 8-, and 9-C); UV (methanol) 206 (ε=4.1×10^4), 240 (s), and 280 (s); MS, *m/z* 227 (M$^+$). Anal. Calcd for $C_{13}H_9NOS$: C, 68.70; H, 3.99; N, 6.16. Found: C, 68.65; H, 3.92; N, 6.10.

*7-Chlorodibenzo[b,f][1,4]thiazepin-11(10H)-one (**2d**).* Mp 300 °C<; IR (KBr) 1645 (s, aromatic amide C=O) and 2900—3300 cm^{-1} (m, complex *N*-H); ^{1}H NMR (Me_2SO-d_6) 400 MHz, δ=7.237 (1H, d, J_{8-9}=8.8 Hz, 9-H), 7.44 (1H, dd, J_{8-9}=8.8 Hz, J_{8-6}=2.3 Hz, 2-H), 7.49 (1H, dd, J_{2-3}=J_{2-1}=7.5 Hz, 2-H), 7.51 (1H, dd, J_{3-2}=J_{3-4}=7.5 Hz, 7-H), 7.54 (1H, d, J_{4-3}=7.5 Hz), 7.689 (1H, d, J_{1-2}=7.5 Hz, 1-H), and 10.774 (1H, s, *N*-H); ^{13}C NMR (Me_2SO-d_6) 400 MHz, δ=131.47, 131.26, 131.10, and 129.61 (1-, 2-, 3-, and 4-H), 138.89 and 135.40 (4a- and 11a-C), 139.01, 128.88, and 137.56 (5a-, 7-, and 9a-C), 131.47, 129.12, and 124.44 (6-, 8-, and 9-C), and 168.00 (C=O); UV (methanol) 208 (ε=4.0×10^4), 245 (s), and 275 nm (s); MS, *m/z* 261 and 263 (M$^+$). Anal. Calcd for $C_{13}H_8NOSCl$: C, 59.66; H, 3.08; N, 5.35. Found: C, 59.58; H, 3.27; N, 5.40.

*7-Cyanodibenzo[b,f][1,4]thiazepin-11(10H)-one (**2e**).* Mp 292—293 °C; IR (KBr) 1660 (s, aromatic amide C=O), 2225 (m, C≡N), and 2900—3300 cm^{-1} (m, complex *N*-H); ^{1}H NMR (Me_2SO-d_6) δ=7.0—8.0 (7H, m, aromatic H) and 10.70 (1H, s, *N*-H); UV (methanol) 206 (3.6×10^4), 220 (s), 258 (2.6×10^4), and 280 nm (s); MS, *m/z* 252 (M$^+$). Anal. Calcd for $C_{14}H_8N_2OS$: C, 66.65; H, 3.20; N, 11.10. Found: C, 66.48; H, 3.05; N, 11.12.

*Preparation of (E)-2-Styryl-1,2-benzisothiazol-3(2H)-one (**9**).* To a mixture of 60 cm^3 of 25% aqueous ammonia and 60 cm^3 of THF was added 12.9 g of 2,2′-dithiobis[benzoyl chloride] in 150 cm^3 of THF at −15 °C over period of

30 min and the solution was stirred for additional 2 h. The solution was concentrated under reduced pressure. The remaining solid was washed with water, cold acetone, and then ether and dried in a desiccator to give 11.4 g of 2,2′-dithiobis[benzamide]: mp 239 °C (dec.); IR (KBr) 3400, 3200, 1640, and 1400 cm^{-1}. To a suspension of 3.8 g of the above compound in 15 cm^3 of carbon tetrachloride was added 2.5 g of bromine in 15 cm^3 of carbon tetrachloride over a period of 10 min. The mixture was stirred overnight, the solvent was evaporated under a reduced pressure and 3 g of sodium hydrogencarbonate in 50 cm^3 of water and 10 cm^3 of THF was added to the resulting residue and the mixture was stirred for 1 h. The solution was concentrated under reduced pressure to give 3.5 g of 1,2-benzisothiazol-3(2*H*)-one: mp 160—161 °C; IR (KBr) 3050, 2900, 2680, 1745, 1635, 1440, and 1325 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.2—8.2 (m); UV (methanol) 203 (ε=1.1×10⁴), 226 (1.6×10⁴), and 316 nm (4.4×10³).

A mixture containing 1.5 g of the above isothiazolone, 1.8 g of phenylacetaldehyde dimethyl acetal, and 10 mg of *p*-toluenesulfonyl chloride was heated at 100 °C for 20 h. The mixture was solidified on cooling to room temperature and the crude solid was purified by chromatography on a silica gel column using benzene as the eluent. The major fraction (2.1 g) obtained was identified as (*E*)-2-styryl-1,2-benzisothiazol-3(2*H*)-one (**9**) on the basis of the following data: mp 145—146 °C; IR (KBr) 1670, 1640, 1450, 1350, 1300, 1265, 1200, 935, and 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.31 (1H, d, J=14.0 Hz), 8.00 (1H, d, J=14.0 Hz) and 7.0—8.2 (9H, m); UV (methanol) 219 (ε=2.3×10⁴), 298 (1.4×10⁴), and 346 nm (1.6×10⁴). Anal. Calcd for $C_{15}H_{11}NOS$: C, 71.12; H, 4.38; N, 5.53. Found: C, 71.45; H, 4.28; N, 5.65.

Photolysis of (E)-2-Styryl-1,2-benzisothiazol-3(2H)-one (9). A solution containing 112 mg (0.44 mmol) of (*E*)-2-styryl-1,2-benzisothiazol-3(2*H*)-one (**9**) in 220 cm^3 of benzene or *t*-butyl alcohol was irradiated using a 450-W Hanovia medium-pressure mercury lamp through a Corex filter sleeve for 30 h. No photoconversion of the starting material was observed by HPLC or TLC. After removing the solvent under reduced pressure to give a solid, the ^1H NMR spectra was identical with that of the starting material **9**.

Photolysis of 2-Aryl-1,2-benzisothiazol-3(2H)-one (1) in the Presence of Oxygen. A solution containing 0.44 mmol of **1** in 220 cm^3 of benzene or methanol with bubbling of oxygen was irradiated through a filter sleeve using a 450-W Hanovia medium-pressure mercury lamp for 2 h. The removal of the solvent under reduced pressure left a light-brown residue which was purified by silica gel chromatography using dichloromethane–hexane as the eluent. Photo-oxidized product **11** was isolated with **2**.

Preparation of 2-Aryl-1,2-benzisothiazol-3(2H)-one 1-Oxide (11). To a solution containing 301 mg (2.25 mmol) of *N*-chlorosuccinimide in 40 cm^3 of dichloromethane was added 2.2 mmol of 2-aryl-1,2-benzisothiazol-3(2*H*)-one in 20 cm^3 of dichloromethane over a period 20 min at 0 °C. The mixture was then stirred for 1 h at room temperature. A solution containing 7 g of potassium hydrogencarbonate in 20 cm^3 of water was added to the reaction mixture and stirred for an additional 1 h. The organic layer was washed with water, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The residual solid was purified by chromatography on silica gel using hexane–ethyl acetate as the eluent. 2-Aryl-1,2-benzisothiazol-3(2*H*)-one 1-oxides (**11a—e**) were obtained in 70—80% yield. The physical and spectral data are as follows:

2-(4-Methoxyphenyl)-1,2-benzisothiazol-3(2H)-one 1-Oxide (11a). Mp 147—148 °C; IR (KBr) 1715 (s, C=O), 1515 (s), 1260 (s, C–O–C, as), and 1100 cm^{-1} (s, S=O); ^1H NMR ($CDCl_3$) δ=3.84 (3H, s, OCH_3), 6.9—8.2 (4H, m), 7.02 and 7.41 (2H and 2H, A_2B_2 quartet, J_{AB}=8.9 Hz); ^{13}C NMR ($CDCl_3$) δ=164.7 (C=O), 128.2 and 145.6 (3a- and 7a-C), 125.1, 126.6, 133.2, and 134.4 (4-, 5-, 6-, and 7-C), 160.0 (1′-C), 129.2 (2′-C), 115.0 (3′-C), 126.1 (4′-C), and 55.5 (OCH_3); UV (methanol) 204 (ε=4.3×10⁴), 226 (1.8×10⁴), and 275 nm (5.8×10³); MS *m/z* 273 (M^+). Anal. Calcd for $C_{14}H_{11}NO_3S$: C, 61.53; H, 4.06; N, 5.13. Found: C, 61.06; H, 3.90; N, 5.03.

2-(4-Methylphenyl)-1,2-benzisothiazol-3(2H)-one 1-Oxide (11b). Mp 167.5—168.5 °C: IR (KBr) 1170 (s, C=O), 1315 (s), and 1100 cm^{-1} (s, S=O); ^1H NMR ($CDCl_3$) δ=2.28 (3H, s. CH_3), and 7.0—8.2 (8H, m); ^{13}C NMR ($CDCl_3$) δ=164.4 (C=O), 128.1 and 145.4 (3a- and 7a-C), 125.0, 126.5, 133.2, and 134.3 (4-, 5-, 6-, and 7-C), 131.0 (1′-C), 127.2 (2′-C), 130.2 (3′-C), 138.8 (4′-C), and 21.1 (CH_3); UV (methanol) 206 (ε=4.3×10⁴), 220 (s), 255 (s), and 275 nm (s); MS, *m/z* 257 (M^+). Anal. Calcd for $C_{14}H_{11}NO_2S$: C, 65.35; H, 4.31; N, 5.44. Found: C, 64.80; H, 4.08; N; 5.29.

2-Phenyl-1,2-benzisothiazol-3(2H)-one 1-Oxide (11c). Mp 136—137 °C; IR (KBr) 1685 (s, aromatic amide C=O) and 1100 (s, S=O); ^1H NMR ($CDCl_3$) δ=7.0—8.2 (m, aromatic-H); ^{13}C NMR ($CDCl_3$) δ=164.3 (C=O), 128.2 and 145.4 (3a- and 7a-C), 125.1, 126.6, 133.3, and 134.5 (4-, 5-, 6-, and 7-C), 133.9 (1′-C), 127.2 (2′-C), 129.6 (3′-C), and 128.8 (4′-C); UV (methanol) 204 (ε=4.29×10⁴) and 270 nm (s); MS, *m/z* 243 (M^+). Anal. Calcd for $C_{13}H_9NO_2S$: C, 64.18; H, 3.73; N, 5.76. Found: C, 63.85; H, 3.56; N, 5.85.

2-(4-Chlorophenyl)-1,2-benzisothiazol-3(2H)-one 1-Oxide (11d). Mp 139—140 °C; IR (KBr) 1720 (s, C=O), 1495 (s), 1310 (s), and 1195 cm^{-1} (s, S=O); ^1H NMR (acetone-d_6) 400 MHz, δ=7.595 and 7.616 (2H and 2H, A_2B_2 quartet J_{AB}=9.2 Hz, 2′- and 3′-H), 7.952 (1H, dt, J_{6-5}=J_{6-7}=8 Hz, J_{6-4}=1.2 Hz, 6-H), 8.024 (1H, dt, J_{5-4}=J_{5-6}=8 Hz, J_{5-7}=1.2 Hz, 5-H), 8.066 (1H, dd, J_{7-6}=8 Hz, J_{7-5}=1.2 Hz, 7-H), and 8.171 (1H, dd, J_{4-5}=8 Hz, J_{4-6}=1.2 Hz, 4-H); ^{13}C NMR (acetone-d_6) δ=164.4 (C=O), 128.1, 145.6 (3a- and 7a-C), 125.3, 126.9, 133.5, and 134.7 (4-, 5-, 6-, and 7-C), 132.7 (1′-C), 128.5 (2′-C), 129.9 (3′-C), and 134.7 (4′-C); UV (methanol) 205 (ε=4.4×10⁴), 225 (s), and 260 (s); MS, *m/z* 277 and 279 (M^+). Anal. Calcd for $C_{13}H_8NO_2SCl$: C, 56.22; H, 2.90; N, 5.04. Found: C, 56.14; H, 2.70; N, 5.07.

2-(4-Cyanophenyl)-1,2-benzisothiazol-3(2H)-one 1-Oxide (11e). Mp 146—147 °C; IR (KBr) 2240 (m, C≡N), 1720 (s, C=O), 1300 (s), and 1090 cm^{-1} (s, S=O); ^1H NMR ($CDCl_3$) δ=7.1—8.2 (m, aromatic-H); ^{13}C NMR ($CDCl_3$) δ=163.9 (C=O), 127.8 and 145.0 (3a- and 7a-C), 125.3, 126.9, 133.8, and 135.1 (4-, 5-, 6-, and 7-C), 138.8 (1′-C), 126.4 (2′-C), 133.4 (3′-C), 118.0 (4′-C), and 111.8 (C≡N); UV (methanol) 208 (ε=4.5×10⁴), 230 (s), 250 (s), and 280 nm (s); MS, *m/z* 268 (M^+). Anal. Calcd for $C_{14}H_8N_2O_2S$: C, 62.68; H, 3.01; N, 10.44. Found: C, 62.52; H, 2.97; N, 10.35.

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