Photoisomerization of 2-Aryl-1,2-benzisothiazol-3(2*H*)-ones

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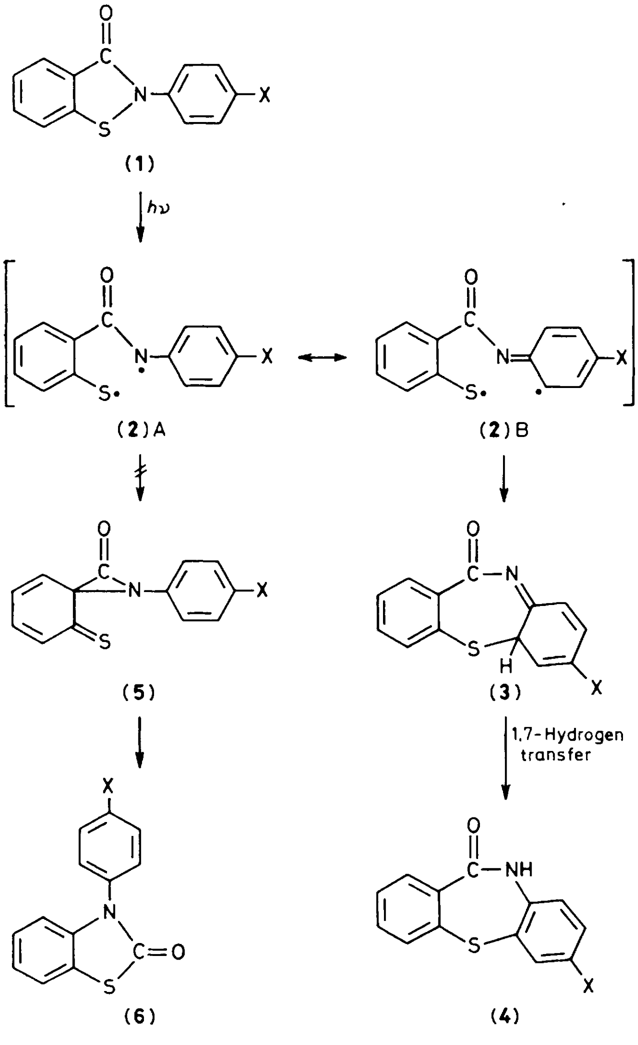
Photoisomerization of the benzisothiazol-3(2*H*)-ones (**1**) gives the dibenzo[*b,f*][1,4]thiazepin-10(11*H*)-ones (**4**) probably *via* homolytic cleavage of the S–N bond [(**1**)→(**2**)], cyclization of the biradical [(**2**)→(**3**)], followed by the formation of an aromatic ring together with 1,7-hydrogen transfer [(**3**)→(**4**)].

Recently we reported the photochemical reactions of *N*-alkyl-*o*-sulphobenzimides in isopropyl alcohol or benzene affording *N*-alkylbenzamides and *N*-alkyl-*o*-phenylbenzamides, respectively in good yield.[1] We describe here the photochemical

Table 1. The photoisomerization of (**1**) to (**4**).

	(**1**) X	Irradiation time/min[a]	Product (**4**)[b] m.p./°C	Yield, %[c]
a	OMe	20	234—235	47
b	Me	60	274—275	57
c	H	90	264—265	31
d	Cl	30	300	13
e	CN	30	292—293	19

[a] Irradiation with a medium pressure 450 W mercury lamp (Hanovia) through a Corex filter ($\lambda > 280$ nm). In the case of (**1a**) and (**1e**) a Vycor filter ($\lambda > 250$ nm) was used. [b] All products were identified by their i.r., ^{1}H n.m.r., and mass spectra and elemental analysis. [c] Yields (isolated) are based on the starting materials consumed.



Scheme 1

behaviour of several 2-substituted benzisothiazol-3(2*H*)-ones (**1**), derivatives of *N*-substituted-*o*-sulphobenzimides reduced on the sulphur atom, which have received much attention in recent years owing to their antibacterial and antifungal properties.[2-4]

2-Arylbenzisothiazol-3(2*H*)-ones (**1**) were prepared according to modified methods in the literature[5] by bromination of *N*,*N'*-diaryl-2,2'-dithiodibenzamides obtained from the reaction of 2,2'-dithiodibenzoyl chloride with aromatic amines. In a typical example, a solution (0.002 M) of 2-(4-methoxyphenyl)benzisothiazol-3(2*H*)-one (**1a**) in 2-methylpropan-2-ol was irradiated under argon gas through a Vycor filter ($\lambda > 250$ nm) with a 450 W medium pressure mercury lamp (Hanovia) for 20 min. After evaporation of the solvent 3-methoxydibenzo[*b*,*f*][1,4]thiazepin-10(11*H*)-one (**4a**) was isolated in 47% yield by elution chromatography on silica gel using hexane–diethyl ether as the eluant. The structure of (**4a**) was assigned on the basis of its spectral and physical properties: m.p. 234—235 °C; i.r. (KBr), 1655(C=O) and 2900—3300 cm^{-1} (complex NH); ^{1}H n.m.r. (400 MHz), δ(CD_3SOCD_3) 3.73 (3H, s, CH_3), 6.95(1H, dd, $J_{2,1}$ 8.8, $J_{2,4}$ 2.9 Hz, 2-H), 7.15(1H, d, $J_{4,2}$ 2.9 Hz, 4-H), 7.11(1H, d, $J_{1,2}$ 8.8 Hz, 1-H), 7.4—7.5(2H, m, $J_{8,9}$ and $J_{7,6}$ 7.3, $J_{7,8}$ 6—7 Hz, 7-H and 8-H), 7.53 (1H, d, $J_{6,7}$ 7.3 Hz, 6-H), 7.68(1H, d, $J_{9,8}$ 7.3 Hz, 9-H), 10.51(1H, s, NH); *m/z* 257(M^+); and satisfactory analytical data were obtained. Similarly, several other 2-arylbenzisothiazol-3(2*H*)-ones (**1b**—**e**) were irradiated to give the ring expanded photoisomers (**4b**—**e**) as summarized in Table 1.

Recently, Rokach and Hamel have reported that the transposition reaction product, 3-phenylthiazol-2(3*H*)-one was formed as the major photoproduct together with a trace amount of benzo[*b*][1,4]thiazepin-4(5*H*)-one on irradiation of 2-phenylthiazol-2(3*H*)-one.[6] However, we detected no such phototransposition reaction product [(**6**)] in the reaction mixtures and (**4**) was the only isolable product. It is of interest that the medium size seven membered ring compounds which are generally very difficult to form were obtained from five membered ring starting materials by an isomerization including the aromatic ring.

The photoisomerization of (**1**) to (**4**) can be explained by the mechanism shown in Scheme 1 involving a homolytic cleavage of the S–N bond to form a biradical intermediate (**2**)A. The biradical (**2**)A forms (**3**) by an intramolecular recombination reaction *via* its resonance form (**2**)B, and finally (**4**) results from photochemical 1,7-hydrogen transfer and the formation of an aromatic ring. The formation of the transposition reaction product (**6**) was not observed and this may be explained by the instability or difficulty of formation of (**5**).

Received, 28th March 1983; Com. 399

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