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Photochemical Reactions of Spiro[benzo[*b*]thiophene-2(3*H*), 1′-cyclopropan]-3-ones

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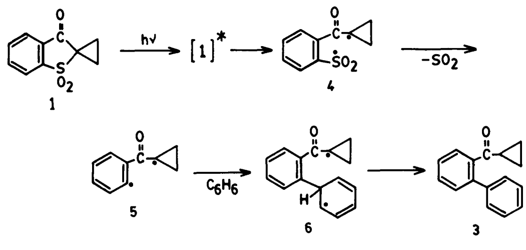
Synopsis. The photolysis of spiro[benzo[*b*]thiophene-2(3*H*),1′-cyclopropan]-3-one 1,1-dioxide (**1**) in benzene afforded 2-biphenylyl cyclopropyl ketone with extrusion of sulfur dioxide, whereas the irradiation of **1** in toluene or *p*-xylene formed photoreduced dimer and bibenzyl or 4,4′-dimethylbibenzyl, respectively. The photolysis of spiro[benzo[*b*]thiophene-2(3*H*),1′-cyclopropan]-3-one in benzene afforded the valence isomer 2,3-dihydro[1]benzothieno[3,2-*b*]furan.

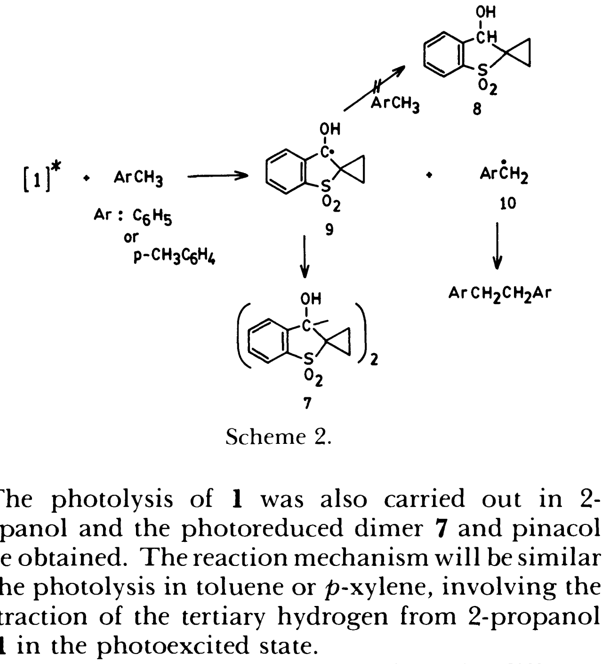
In recent years, considerable attention has been focused on the photochemistry of five-membered heterocyclic ring systems.[1] We reported that the photochemical reactions of 2-aryl-1,2-benzisothiazol-3(2*H*)-ones in benzene give dibenzo[*b,f*][1,4]thiazepin-10(11*H*)-ones,[2] whereas the photolyses of 2-substituted 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxides in benzene give *N*-substituted *o*-phenylbenzamides with extrusion of sulfur dioxide.[3] In our systematic investigations of photochemical reactions of benzisothiazoles and their analogues, we wish to report here the photochemical behavior of spiro[benzo[*b*]thiophene-2(3*H*),1′-cyclopropan]-3-one 1,1-dioxide (**1**) and spiro[benzo[*b*]-thiophene-2(3*H*),1′-cyclopropan]-3-one (**2**). These are expected to be photoreduced at the carbonyl group and to break their bonds at spiro carbon-sulfur atom or at the highly-strained three membered ring.

When a solution containing of **1** in benzene was irradiated under argon with light of wavelength >280 nm, an extremely clean conversion to a single photoproduct occurred. This product was deduced to be 2-biphenylyl cyclopropyl ketone (**3**) on the basis of its straightforward spectral properties (see experimental section). The reaction is quite similar to the photoreactions of 2-substituted 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxides in benzene,[3] and hence the reaction could be accounted for by a homolytic process *via* radical intermediates **4**, **5**, and **6**, as shown in Scheme 1.



Scheme 1.

Meanwhile, when **1** was irradiated in toluene or *p*-xylene photoreduced dimer, 3,3″-bi[spiro[benzo[*b*]-thiophene-2(3*H*),1′-cyclopropane]]3,3″-diol 1,1,1″,1″-tetraoxide (**7**) was formed with bibenzyl or 4,4′-dimethylbibenzyl, respectively, in good yield. No detectable quantities of such photoreduced alcohol as spiro[benzo[*b*]thiophene-2(3*H*),1′-cyclopropan]-3-ol 1,1-dioxide (**8**) could be observed in the reaction mixture. The photoreaction of **1** in these solvents suggests that **1** in the photoexcited state abstracts the hydrogen atom from the methyl group of toluene or *p*-xylene to give radical **9** and benzyl (or *p*-methylbenzyl) radical (**10**) faster than a homolytic cleavage to **4** occurs. The absence of the alcohol **8** suggests that radical **9** has no ability to abstract the hydrogen atom from the methyl group of toluene or *p*-xylene and survive until a coupling reaction occurs to give dimer **7** (Scheme 2).



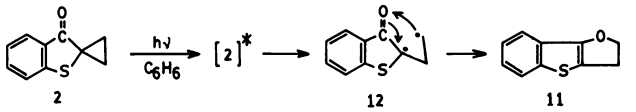
Scheme 2.

The photolysis of **1** was also carried out in 2-propanol and the photoreduced dimer **7** and pinacol were obtained. The reaction mechanism will be similar to the photolysis in toluene or *p*-xylene, involving the abstraction of the tertiary hydrogen from 2-propanol by **1** in the photoexcited state.

The photoreaction of **1** behaved in quite different manners in benzene, and in toluene, *p*-xylene, or 2-propanol. **1** in the photoexcited state abstracts a hydrogen when the solvents are hydrogen donating, whereas in benzene **1** cleaves the C–S bond homolytically, affording radical intermediates **4** and **5**. The photoreaction of 2-substituted 1,2-benzisothiazol-3(2*H*)-ones in benzene or 2-propanol, however, always included the extrusion of sulfur dioxide.[3] It is also noteworthy that **7** is the sole photoreduced product and no formation of any product like **8** is observed in the photolysis of **1**, in contrast to the reported photoreactions of phthalimides.[4]

The photoreaction of **2** in benzene afforded 2,3-dihydro[1]benzothieno[3,2-*b*]furan (**11**) as the only isolable product. The reaction mechanism will be accounted for by the homolytic reaction shown in Scheme 3.

In this case, the reaction seems to proceed *via* the homolytic cleavage of the strained cyclopropane ring affording radical **12** and the following ring construction to give **11**. The photolysis of **2** in toluene



Scheme 3.

or *p*-xylene did not form any isolable product in spite of the starting material was consumed.

Experimental

Measurements. Melting points are uncorrected. IR and UV spectra were determined on a Hitachi EPI-G2 and a Hitachi 220A spectrophotometer. The proton magnetic spectra were recorded at 60 MHz by using a Hitachi R-20B spectrometer with TMS as an internal standard in $CDCl_3$. Mass spectra were determined with a JMS-DX300 high resolution mass spectrometer. Elemental analyses were carried out by using a Perkin-Elmer 240 elemental analyzer.

Materials. Spiro[benzo[*b*]thiophene-2(3*H*),1′-cyclopropan]-3-one (**2**) was prepared from *o*-mercaptobenzoic acid (15.4 g) and α-bromo-γ-butyrolactone (20.6 g) according to the method described in the literature:[5] yield 10.5 g (65%) as colorless prisms form hexane–dichloromethane, mp 69—70°C (lit, mp 70°C).[6] IR (KBr) 1680, 1590, 1450, 1320, 1080, 980, and 740 cm^{-1}; NMR ($CDCl_3$) δ 1.3—1.9 (4H, m) and 7.2—7.9 ppm (4H, m); UV (EtOH) 367 (ε=2.67×10^3), 350 (2.60×10^3), 267 (5.50×10^3), 258 (6.58×10^3), 237 (3.36×10^4), and 208 nm (1.29×10^5). Spiro[benzo[*b*]thiophene-2(3*H*),1′-cyclopropan]-3-one 1,1-dioxide (**1**) was prepared by the oxidation of **2** (5.2 g) with 13.7 g of perbenzoic acid in dichloromethane at 0°C: yield 5.6 g (91%) as colorless prisms from hexane–dichloromethane, mp 198—199°C (lit, mp 202°C).[6] IR (KBr) 1720, 1590, 1460, 1315, 1300, 1155, and 990 cm^{-1}; NMR ($CDCl_3$) δ 1.30—2.00 (4H, m) and 7.40—8.10 ppm (4H, m); UV (MeOH) 292 (ε=6.55×10^2), 283 (7.74×10^2), 246 (9.64×10^3), and 210 nm (3.35×10^4).

Photolysis of 1 in Benzene. A solution containing 200 mg of **1** in 220 cm^3 of benzene was irradiated under argon with a 450W medium-pressure mercury lamp (Hanovia) through a Corex filter sleeve for 8 h. Removal of the solvent under reduced pressure left a pale-yellow oil which was subjected to the chromatography on silica gel, using benzene as the eluent. 2-Biphenylyl cyclopropyl ketone (**3**) was isolated (130 mg, 86%)[7] with 58 mg of unreacted starting material **1**. The structure of **3** was assigned based on the following data: mp 81—82°C (from hexane); IR (KBr) 3020, 1670, 1595, 1450, 1435, 1280, 1040, and 990 cm^{-1}; NMR ($CDCl_3$) δ 0.50—0.72 (2H, m), 1.00—1.16 (2H, m), 1.64—1.88 (1H, m), 7.56 (5H, s), and 7.48—7.78 ppm (4H, m); Mass (20 eV) *m/z* 222 (M^+), 194, 165, 153, 69, and 41. Found: C, 86.39; H, 6.23%. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35%.

Photolysis of 1 in Toluene. A solution containing 200 mg of **1** in 220 cm^3 of toluene was irradiated under argon through a Pyrex filter sleeve for 18 h. After removal of the solvent, the photolysate was subjected to the chromatography on silica gel using a 2:1 hexane–ether mixture as the eluent to give bibenzyl (62 mg, 71%) and **7** (140 mg, 70%). The structure of bibenzyl was verified by comparison with an authentic sample, and that of **7** was identified on the basis of the following data: mp 276°C (decomp); IR (KBr) 3450, 3030, 1600, 1495, 1455, 1290, 1180, 1165, 1155, 1120, 1100, 1060, 1050, and 980 cm^{-1}; NMR (CD_3SOCD_3) δ 0.91—1.6 (4H, m), 6.8—8.2 ppm (4H, m); Mass *m/z* 418 (M^+), 362, 314, 209, 152, 136, 104, and 76. Found: *m/z* 209.02719. Calcd for $C_{10}H_9O_3S$: *m/z* 209.02719.

Photolysis of 1 in p*-Xylene.* A solution containing 200 mg of **1** in 220 cm^3 of *p*-xylene was irradiated under argon through a Pyrex filter sleeve for 18 h. After evaporation of the solvent, the photolysate was subjected to the chromatography on silica gel using a hexane–ether mixture as the eluent to give 4,4′-dimethylbibenzyl (78 mg, 77%) and **7** (150 mg, 75%). The structure of 4,4′-dimethylbibenzyl was verified by comparison with an authentic sample.

Photolysis of 1 in 2-Propanol. A solution containing 200 mg of **1** in 220 cm^3 of 2-propanol was irradiated under argon through a Pyrex filter sleeve for 16 h. After removal of the solvent, the photolysate was subjected to the chromatography on silica gel using a hexane–ether as the eluent to give pinacol (41 mg, 72%) and **7** (157 mg, 78%).

Photolysis of 2 in Benzene. A solution containing of 200 mg of **2** in 220 cm^3 of benzene was irradiated under argon through a Pyrex filter for 2 h. Removal of the solvent under reduced pressure left a dark oil which was purified by thick-layer (preparative thin layer) chromatography using a 1:1 mixture of dichloromethane–benzene as the eluent. **11** (9.7 mg, 9%)[7] was isolated with 93 mg of unreacted starting material. The structure of **11** was identified by comparison with an authentic sample.[8]

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