Photochemistry of Pesticides, 12 [1]

On the Photoconversion of 1,3-Dihydro-2H-benzimidazole-2-thione, 2(3H)-Benzothiazolethione, and 2-Chlorobenzothiazole

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1,3-Dihydro-2H-benzimidazole-2-thione, 2(3H)-Benzothiazolethione, 2-Chlorobenzothiazole. Photodegradation. Photooxidation

The photoreactivity of 1,3-dihydro-2H-benzimidazole-2-thione (la) and 2(3H)-benzothiazolethione (lb) has been studied in several solvents in the presence of oxygen or without methylene blue as a sensitizer. The corresponding disulfides (5a, b), 2-oxo derivatives (2a, b), benzimidazole and benzothiazole (11a, b), and elemental sulfur have been characterized as the main products. The UV irradiation of the disulfides 5a, b results in the formation of the same product pattern as the thiones la, b. Photolysis of 2-chlorobenzothiazole (12) in acetonitrile gives a mixture of 2b, 2,2'-dibenzothiazole (13), while photolysis of 12 in ethanol yields 2b and 1b. Products and mechanisms are discussed and compared with previous studies in this area.

Introduction

1,3-Dihydro-2H-benzimidazole-2-thione (named earlier: 2-mercaptopbenzimidazole) (la) and 2(3H)-benzothiazolethione (named earlier: 2-mercaptopbenzothiazole (lb)), the latter marketed under the names MBT, Captax, Dermacid, Mertax, and Thiotax, have both found broad applications as rubber vulcanization accelerators, antioxidants, corrosion inhibitors, and heat stabilizers. Additionally, la is biologically active [3], especially as a herbicide [3b]; lb has further applications as a fungicide, a bactericide, a disinfectant, and a wood preservative [4].

Crank and Mursyidi have reported in 1982 [5] that the UV irradiation of “2-mercaptobenzimidazole” (la) in the presence of air (oxygen) leads to benzimidazole sulfate (8a) as a sole reaction product. Irradiation in acetonitrile gave 8a and traces of bis-(2-benzimidazolyl)-disulfone (6a). Moreover, UV irradiation of “2-mercaptobenzothiazole” (lb) in ethanol, methanol or acetonitrile resulted in the isolation of the benzothiazole analogs 6b and 8b. Carrying out the UV irradiation of lb in benzene produced bis-(2-benzothiazolyl)-disulfide (5b), as well as 6b and 8b (cf. Scheme 2). It has been further claimed that the disulfides 5a, b and disulfones 6a, b are intermediates and must be precursors of the major products 8a, b. Both oxygen and water have been found to be essential for completion of the photo-reactions.

These contradictory results [5, 6] which have attracted our interest and the fact that recently we have...
Results and Discussions

We have likewise irradiated an 1% acetonitrile, ethanol, or benzene solution of 1a with a Hg-high pressure lamp in a Pyrex reactor (λ > 313 nm) while oxygen (or normal air) was steadily circulated into the mixture with a moderate rate, the reaction course being monitored by TLC. After ca. 100 h irradiation time, the photolysate was carefully chromatographed over silica gel to give products 2a, 5a, 11a, and elemental sulfur. The identities of the products were confirmed by comparison with authentic specimens (cf. Scheme 3 and Experimental).

In a considerably extended irradiation experiment (up to 350 h), we noted an appreciable increase in the yields of 2a and 11a, while the ratio of formation of thiole 1a vs. disulfide 5a remained constant. Carrying out the photolysis of 1a in the presence of a sensitizer (methylene blue) does not cause any qualitative changes in the product composition or yield.

Photolysis of 2(3H)-benzothiazolethione (1b) in acetonitrile, ethanol or benzene (best results in acetonitrile) for 120 h, gave a pattern of products similar to that obtained from the π-isoelectronic 1a. The products, in the order eluted from the chromatography column are: benzothiazole (11b) (5.6%), elemental sulfur (9.7%), 2(3H)-benzothiazolethione (1b) (20.8%), bis-(2-benzothiazolyl)-disulfide (5b) (32%), and 2(3H)-benzothiazalone.
A mechanism that accounts for the formation of the obtained photoproducts derived from the photolysis of the title compounds 1a, b is presented in Scheme 3. Thus, upon UV irradiation, 1a, b cleave at the sulfur-hydrogen bond. Subsequent recombination of the thyl radicals formed leads to the disulfides 5a, b [9, 10], which also have been proposed and identified as intermediates in the previous work [6]. Upon UV irradiation of the disulfides 5a, b, besides the retro-S–S-cleavage into 2 thyl radicals 9a, b [9, 10], another homolysis can be discussed leading to 2-benzimidazolyl and 2-benzothiazolyl radicals (10a, b) and the appropriate disulfan radicals (10’a, b); this type of competitive carbon-sulfur cleavage has been discussed earlier [11] for the photoreaction of disulfides. Radicals 10a, b afford in turn benzimidazole and benzothiazole 11a, b via hydrogen abstraction, while, by oxygen attack on 10a, b, 1,3-dihydro-2H-benzimidazole-2-one and 2(3H)-benzothiazolone (2a, b) are formed, 2a being mentioned in lit. [5]. On the other hand, disulfane radicals (10’a, b) can break down into elemental sulfur and 1a, b after H-transfer. Both photolysis pathways 5a, b → 9a, b → 1a, b and 5a, b → 10’a, b → 1a, b offer plausible explanations for the observation of starting materials 1a, b found in the photolyses even after a long period of UV irradiation (e.g. 350 h), i.e. there seems to exist a steady equilibrium between photoproducts and starting materials (1a, b ⇋ 5a, b ⇋ 9a, b ⇋ 1a, b).

These results are unambiguously supported by independent synthesis of the disulfides 5a, b and their UV irradiation. In all cases, the photolyses contain besides starting materials 1a, b (unchanged or formed) the products 2a, b, 11a, b, and elemental sulfur.

Although the effect of an added sensitizer seems to be negligible, due to the rapid formation of disulfides 5a, b which might act as quenchers for singlet oxygen [12], a direct transformation 1a, b → 2a, b with residual traces of singlet oxygen cannot be excluded, since there are many C=S→C=O exchange reactions reported for thiones after treatment with singlet oxygen [13].

These results allow interesting conclusions to be drawn. Thus, considering the earlier report [5], we have been able to isolate products 2a, b, 11a, b, and elemental sulfur, however, in our experiments, the formation of cyanoguanidine (4) turned out to be irreproducible. As a consequence we assume a different reaction course leading primarily to 5a, b. Regarding the recent work cited [6] we can now confirm that upon photolysis of 1a, b the disulfides 5a, b are in fact intermediates as well as main photoproducts but, on the other hand, we were unable to obtain the sulfones 6a, b or the hydrosulfates 8a, b [6].

As stated in the earlier communication [6], the sulfates are considered the main products besides the disulfones 6a, b. This seems in our opinion and on the basis of our experimental results unlikely for the following reasons:

(a) the known unstability of the hygroscopic benzimidazole sulfate (8a) [14] as well as the facile decomposition of the benzothiazole sulfate (8b) [15] in the presence of water, and the reported remark [6] that the presence of water in the solution is essential for completion of the reaction are, from our viewpoint, contradictory;

(b) the structure and data attributed to the benzothiazole sulfate (8b) are based upon an elemental formula C$_7$H$_7$NS·H$_2$SO$_4$ [6], however, the correct elemental composition has been stated in 1936 to be C$_7$H$_7$NS·H$_2$SO$_4$·H$_2$O [15], since it has been reported that attempts to dehydrate this hydrate led to its decomposition [15];

(c) the disulfones (6a, b) have been reported to be extremely insoluble [6]; upon careful work-up of our reaction mixtures, we were unable to detect any significant amounts of these compounds.

The close inter-relationship in the behaviour of 2(3H)-benzothiazolethione (1a) and 1,3-dihydro-2H-benzimidazole-2-thione (1b) upon UV irradiation induced us also to investigate the photolysis of 2-chlorobenzothiazole (12), to determine if 12 behaves in a fashion similar to the previously [5] reported 2-chlorobenzimidazole. Thus, the photolysis of an 1% air-saturated (or oxygen circulated) acetonitrile solution of 12 resulted in the disappearance of 12 (TLC) after ca. 50 h. The photolysate was separated on silica gel, and 2(3H)-benzothiazolone (2b) (16.8%) and the symmetric dimer 2,2’-dibenzo-thiazole (13) (37.5%) were obtained as the photoproducts (cf. Scheme 4).

The photoreaction proceeds, however, very sluggishly in air saturated ethanol, whereby only 2b (33.6%) and benzothiazole (11b) (11%) were isolated after 120 h irradiation time. The identities of

(2b) (20.5%). Again, all products were unambiguously established by comparisons with authentic samples.
2b and 13 [16] were established by comparison of m.p. and spectral data with those of authentic samples (cf. Experimental).

With regard to the photodissociation step and the formation of the 2-oxo derivative (2b), this photolysis mechanism parallels the reaction course of 2-chlorobenzimidazole [5]. However, 2,2’-dibenzothiazole (13) is generated in a different manner, by simple recombination of two benzothiazolyl radicals. The formation of 2,2’-dibenzoimidazole has not yet been observed. 13 has been obtained by Grellmann and Tauer [16] by photodehydrodimerization of benzothiazole in air saturated acetonitrile.

Experimental

Melting points: uncorrected. — Elemental analyses: Analytical Laboratory of the Institute. — IR spectra: Perkin-Elmer 157-G (in KBr or CHCl₃). — ¹H NMR: Bruker WH-90 (δ-values, TMS as internal standard). — MS: MS-50 of Kratos (A.E.I.). The photolyses were carried out in a Pyrex photoreactor equipped with a high-pressure Hg-lamp (Philips HPK 125). — The TLC system used was toluene/ethyl acetate/ethanol 6:3:1 (v/v/v). — 1a, b and 12 are commercially available.

Photolyses experiments

(a) UV irradiation of 1,3-dihydro-2H-benzimidazole-2-thione (1a): A solution of 1a (2.5 g, 16 mmol) in acetonitrile, ethanol, or benzene (250 ml) (best results in acetonitrile), was irradiated for 100 h, while a steady stream of oxygen (or normal air) was circulated into the mixture with a moderate rate. After evaporation of the solvent in vacuo, the mixture was separated by column chromatography on silica gel with light petroleum ether (40–60 °C), and employing the eluent systems: toluene, toluene-ethyl acetate, and finally toluene/ethyl acetate/ethanol.

Fraction (up to 8:2) eluted 42 mg (16%) of yellow needles, m.p. 119–122 °C, identified as elemental sulfur (TLC, MS).

Fraction (up to 6:4) contained 448 mg (18%) of starting material 1a, m.p. 302 °C (methanol; lit. m.p. 302–304 °C [17]); MS: m/z 150 (M⁺).

Fraction (up to 4:6) afforded 669 mg (27%) of a yellow crystalline product, which proved to be bis-(2-benzimidazolyl)-disulfide (5a), m.p. 227 °C (ethanol, lit. m.p. 230 °C [18]); MS: m/z 298 (M⁺).

Fraction (up to 6:3:1) gave 78 mg (8%) of colorless crystals m.p. 168 °C, identified as benzimidazole (11a) (ethanol, lit. m.p. 171–172 °C [19]); MS: m/z 118 (M⁺).

Finally, fraction eluted with (4:4:2) yielded 167 mg (15%) of colorless material shown to be 1,3-dihydro-2H-benzimidazole-2-one (2a), m.p. 310 °C (methanol, lit. m.p. 309–312 °C [20]); MS: m/z 134 (M⁺).

Similar results have been obtained, when 1a was irradiated in the presence of singlet oxygen (the solution contained 30 mg of methylene blue, and oxygen was steadily circulated into the solution with moderate rate). When the photoreaction of 1a was carried out in acetonitrile, similar to the procedure described above but for a longer reaction time (ca. 350 h), it resulted in the isolation of sulfur (55 mg, 20.8%). 1a (322 mg, 12.8%), 5a (602 mg, 24.2%), 11a (72 mg, 7.4%), and 2a (245 mg, 22%).

(b) UV irradiation of 2(3H)-benzothiazolethione (1b): The photoconversion of 1b (2.5 g, 14 mmol) in acetonitrile, ethanol, or benzene (250 ml) (best results in acetonitrile for 120 h) was carried out as de-
scribed for 1a. The photolysate was worked up in the usual manner employing toluene and then toluene ethyl acetate as the developing system.

Fraction (up to 9:1) furnished 56 mg (5.6%) of a pale yellow liquid, identified as benzothiazole (11b) (comparative IR and 1H NMR spectra [21]); MS: m/z 135 (M+).

Fraction (8:2) contained 23 mg (9.7%) of a yellow crystalline material, m.p. 120—122 °C, proved to be elemental sulfur (TLC, MS).

Fraction (up to 6:4) yielded 522 mg (20.8%) of 2(3H)-benzothiazolethione (1b), m.p. 179 °C (methylenechloride, lit. m.p. 177—180 °C [22]); MS: m/z 167 (M+).

Fraction (5:5) produced 793 mg (32%) of a pale yellow material, m.p. 180 °C, shown to be bis-(2-benzothiazolyl)-disulfide (5b) (ethanol, lit. m.p. 180 °C [23]); MS: m/z 332 (M+).

Finally, elution with pure ethyl acetate yielded 231 mg (20.5%) of colorless material, m.p. 128 °C, which was identified as 2(3H)-benzothiazolone (2b) (ethanol, lit. m.p. 128—130 °C [24]); MS: m/z 151 (M+).

(c) UV irradiation of bis-(2-benzimidazolyl)-disulfide (5a): The disulfide 5a was prepared according to the method of Knobloch and Rintelen [18] and UV irradiated (2.5 g, 83 mmol) in acetonitrile (250 ml) similar to the photolysis of 1a for 120 h. The reaction mixture was worked up and the crude photoproduce separated by column chromatography. Elution and identification of the products exactly matched the compounds isolated in the photolysis of 1a, namely: Elementar sulfur: 65 mg (24.4%); 1,3-dihydro-2H-benimidazol-2-thione (1a): 140 mg (11.2%); starting material 5a: 392 mg (15.7%); benzimidazole 11a: 85 mg (8.6%); 1,3-dihydro-2H-benzimidazole-2-one (2a): 235 mg (21.0%).

(d) UV irradiation of bis-(2-benzothiazolyl)-disulfide (5b): The disulfide 5b was prepared as described previously [23], and then (2.5 g, 7.5 mmol) UV irradiated in acetonitrile or ethanol in a manner similar to the photolysis of 1a, for 120 h. The photolysate was worked up in the usual way and gave a pattern of products exactly matching the compounds isolated in the photolysis of 1b with the following yields:

Benzothiazole 12b: 69 mg (6.8%); elemental sulfur: 34 mg (14.2%); 2(3H)-benzothiazolethione (1b): 367 mg (29.2%); bis-(2-benzothiazolyl)-disulfide (5b): 425 mg (17.0%); 2(3H)-benzothiazolone (2b): 341 mg (30.0%).

(e) UV irradiation of 2-chlorobenzothiazole (12): 2-Chlorobenzothiazole (12) (2.5 g, 15 mmol) in acetonitrile (250 ml) was irradiated using the same procedure as described in (a). The reaction course was monitored by TLC, which indicated the disappearance of 12 after ca. 50 h. The photolysate was worked up in the formentioned way and the chromatography was carried out with toluene with increasing amounts of ethyl acetate.

Fraction (5:5) gave 743 mg (37.5%) of colorless material shown to be 2,2'-dibenzothiazole 13, m.p. 300 °C (methanol, lit. m.p. 300—304 °C [16, 25]); MS: m/z 268 (M+).

Pure ethyl acetate afforded 373 mg (16.8%) of colorless material m.p. 128 °C, identified as 2(3H)-benzothiazolone (2b) (ethanol, lit. m.p. 128—130 °C [24]); MS: m/z 151 (M+).

Photolysis of 12 (2.5 g, 15 mmol) in ethanol (250 ml) for 120 h, was carried out as described above; only benzothiazole (11b) (218 mg, 11.0%) and 2(3H)-benzothiazolone (2b) (748 mg, 33.6%) were isolated.

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