

Photoisomerization of Some 2-Alkylthiobenzothiazoles

A. GÁPLOVSKÝ, R. HERCEK, and P. KURÁŇ

Institute of Chemistry, Comenius University,
SK-842 15 Bratislava
e-mail: gaplovsky@fns.uniba.sk

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Photolysis of 2-benzylthio-, 2-diphenylmethylthio-, 2-allylthio-, 2-(methoxycarbonylmethylthio)-, 2-(1-naphthylmethylthio)-, and 2-(2-naphthylmethylthio)benzothiazole (*Ia–If*) was studied. Photoreactivity of these compounds was dependent on the type of the alkyl moiety as well as on the energy of applied radiation. The main products of photolysis of studied benzothiazoles were the corresponding 3-alkyl-3*H*-benzothiazole-2-thiones (*Iia–Iif*) and 3*H*-benzothiazole-2-thione (*III*). The ratio between these two groups of formed thioketones *Iia–Iif* and *III* was dependent on the character of the substituent in position 2 of the benzothiazole skeleton. Benzothiazole (*IV*) and products formed by dimerization of radicals derived from substituent were the other products of photolysis. The predominant formation of the corresponding *Iia* and *Iib* was observed with *Ia* and *Ib* only. For all studied thioethers except of *Ic* an irreversible photoisomerization was observed. An increase of yield of *III* on account of *Iia–Iif* was found after sensitized photolysis of thioethers *Ia–If* ($\lambda_{\text{irr}} > 290 \text{ nm}$).

The results of the previous paper [1] led to the conclusion that photoreactivity of 2-alkylthiobenzothiazoles is considerably dependent on the character of substituents in position 2 of benzothiazole skeleton. We observed that relatively small change in the structure of substituents in position 2 may substantially alter the yield as well as the course of photochemical transformations. A good example for this is significant difference in photoreactivity of 2-methylthio- and 2-benzylthiobenzothiazole. In order to understand better observed differences we have decided to investigate the photoreactivity of 2-alkylthiobenzothiazoles having substituents with one or more double bonds in position 2. The main objective of our effort was to study a photochemical reactivity and possibility of photochemical isomerization of 2-alkylthiobenzothiazoles in dependence on the structure and reaction conditions and to compare their photoreactivity with that of 2-benzylthiobenzothiazole.

EXPERIMENTAL

2-Alkylthiobenzothiazoles and 3-alkyl-3*H*-benzothiazole-2-thiones were prepared according to literature (*Ia*, m.p. = 41–42 °C [2], *Ib*, m.p. = 108–109 °C [3], *Ic*, b.p. = 178–181 °C at 101.32 kPa [2], *Id*, m.p. = 74–76 °C [4], *Iia*, m.p. = 149–150 °C [2], *Iic*, m.p. = 65–67 °C [2], *Iid*, m.p. = 122–124 °C [5]).

2-(1-Naphthylmethylthio)- (*Ie*) and 2-(2-naphthylmethylthio)benzothiazole (*If*) were prepared by alky-

lation of sodium salt of 3*H*-benzothiazole-2-thione with corresponding alkylhalogenides according to general procedure [2, 6, 7].

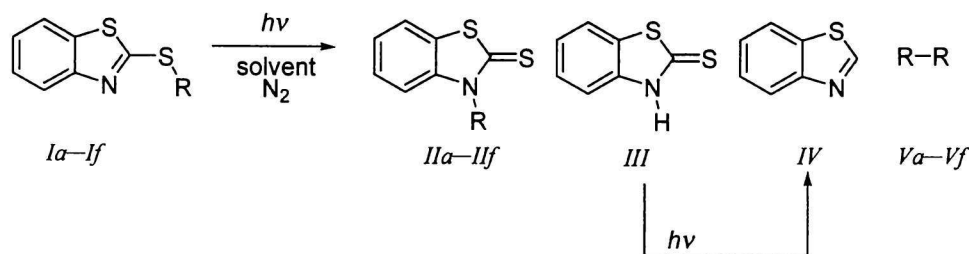
2-(1-Naphthylmethylthio)benzothiazole (*Ie*): m.p. = 77–78 °C. For $\text{C}_{18}\text{H}_{13}\text{NS}_2$ ($M_r = 307.4$) $w_i(\text{calc.})$: 70.36 % C, 4.23 % H, 4.56 % N, 20.86 % S; $w_i(\text{found})$: 70.68 % C, 4.23 % H, 4.60 % N, 20.50 % S. $^1\text{H NMR}$ spectrum (CDCl_3), δ : 5.1 (s, 2H, $-\text{CH}_2-\text{Ph}$); 7.26–8.09 (m, 11H, naphthyl and benzothiazole rings).

2-(2-Naphthylmethylthio)benzothiazole (*If*): m.p. = 78–80 °C. For $\text{C}_{18}\text{H}_{13}\text{NS}_2$ ($M_r = 307.4$) $w_i(\text{calc.})$: 70.36 % C, 4.23 % H, 4.56 % N, 20.86 % S; $w_i(\text{found})$: 70.60 % C, 4.22 % H, 4.61 % N, 20.63 % S. $^1\text{H NMR}$ spectrum (CDCl_3), δ : 4.77 (s, 2H, $-\text{CH}_2-\text{Ph}$); 7.25–7.91 (m, 11H, naphthyl and benzothiazole rings).

3-Alkyl-3*H*-benzothiazole-2-thiones *Iib*, *Iie*, and *Iif* were prepared from the corresponding 3-alkyl-3*H*-benzothiazole-2-ones and $\text{P}_4\text{S}_{10}/\text{Na}_2\text{CO}_3$ according to general procedure [8]. The crude thioketones were purified by column chromatography on silica gel (eluents: 3-methylpentane, benzene).

3-Diphenylmethyl-3*H*-benzothiazole-2-thione (*Iib*): m.p. = 160–162 °C. For $\text{C}_{20}\text{H}_{15}\text{NS}_2$ ($M_r = 333.5$) $w_i(\text{calc.})$: 71.9 % C, 4.5 % H, 4.19 % N; $w_i(\text{found})$: 72.2 % C, 4.8 % H, 4.35 % N. $^1\text{H NMR}$ spectrum (CDCl_3), δ : 5.89 (s, 2H, $\text{CH}(\text{Ph})_2$); 7.02–7.60 (m, 14H, phenyl and benzothiazole).

3-(1-Naphthylmethyl)-3*H*-benzothiazole-2-thione (*Iie*): m.p. = 212–214 °C. For $\text{C}_{18}\text{H}_{13}\text{NS}_2$ ($M_r = 307.4$) $w_i(\text{calc.})$: 70.3 % C, 4.2 % H, 4.6 % N;



Scheme 1

w_i (found): 69.2 % C, 4.2 % H, 4.3 % N. 1H NMR spectrum ($CDCl_3$), δ : 6.16 (s, 2H, —N—CH₂); 6.83—8.15 (m, 11 H, naphthyl and benzothiazole).

3-(2-Naphthylmethyl)-3H-benzothiazole-2-thione (IIIf): m.p. = 171—173 °C. For $C_{18}H_{13}NS_2$ ($M_r = 307.4$) w_i (calc.): 70.3 % C, 4.2 % H, 4.6 % N; w_i (found): 69.6 % C, 4.2 % H, 4.3 % N. 1H NMR spectrum ($CDCl_3$), δ : 5.85 (s, 2H, —N—CH₂); 7.22—7.79 (m, 11H, naphthyl and benzothiazole).

The phototransformations were monitored by UV VIS spectroscopy on an HP 8452 (Hewlett—Packard) diode-array spectrophotometer. Reaction mixtures were analyzed by HPLC (Waters) and GC/MS/FID HP 5890 Series II (Hewlett—Packard) system. Individual compounds were identified by mass spectra and quantified by comparison with authentic samples. 1H NMR spectra were measured in $CDCl_3$ solution on a GEMINI (Varian) instrument at 300 MHz with tetramethylsilane as an internal standard. Fluorescence spectra of thioethers *Ia—If* dissolved in heptane and methanol were measured on a spectrofluorimeter F-2000 (Hitachi). The melting points were measured with a Kofler micro hot-stage.

Photolysis

Irradiations were carried out in Simax tubes (10 cm³) (for $\lambda_{irr} = 253.7$ nm, quartz tubes) closed with the Teflon stopcocks by 125 W medium-pressure or 16 W low-pressure mercury lamps (Applied Photo-physics).

Solutions of studied thioethers *Ia—If* or thioketones *IIa—IIIf* ($c = 10^{-3}$ mol dm⁻³) in methanol, benzene, and n-heptane were purged with nitrogen for 30 min before irradiation. Sensitized photolyses were performed in nitrogen atmosphere with acetone as solvent. Under such circumstances predominant absorption of sensitizer was fulfilled.

RESULTS AND DISCUSSION

For studied thioethers *Ia—Id* with the exception of naphthylmethyl derivatives *Ie* and *If* the absence of fluorescence emission was observed in spite of the fact that the character of UV VIS spectra of all studied compounds does not differ. From comparison of fluorescence spectra of derivatives *Ie*, *If* and

1-methylnaphthalene it follows that the origin of observed fluorescence emission is naphthalene moiety. A decrease of fluorescence quantum yields of derivatives *Ie* and *If* ($\Phi_F = 2-9 \times 10^{-3}$) in comparison with the quantum yield of 1-methylnaphthalene ($\Phi_F = 0.49$) [9] was also found. This fact is caused probably by the more effective deactivation of S₁ state of studied thioethers *Ie* and *If* through the different deactivation channels (*e.g.* photoreactivity, radiationless decay) than by means of fluorescence emission.

A general feature of direct photolysis of 2-alkylthiobenzothiazoles *Ia—If* was the cleavage of C—S bonds. This cleavage is characteristic of the primary photochemical step of thioethers [10] and in the photolysis of compounds *Ia—If* can be realized in case of substituent—sulfur or benzothiazole—sulfur bonds.

We can conclude according to the results given in Table 1 that in studied thioethers the substituent—sulfur bond is preferentially cleaved. The separation of formed radical pairs after C—S bond cleavage leads to the formation of 3*H*-benzothiazole-2-thione (*III*) (Scheme 1) (product of abstraction of hydrogen atoms from medium by benzothiazol-2-ylsulfanyl radicals) and radicals derived from the substituents. The latter can undergo a dimerization, especially in the absence of oxygen. Thus the formation of 1,2-diphenylethane (*Va*), dimethyl succinate (*Vd*), 1,2-bis(1-naphthyl)ethane (*Ve*), and 1,2-bis(2-naphthyl)ethane (*Vf*) was observed (Table 1).

Another interesting feature of the photolysis of 2-alkylthiobenzothiazoles *Ia—If* was photochemical migration of the substituent from position 2 to position 3 of benzothiazole skeleton, under the formation of the corresponding 3-alkyl-3*H*-benzothiazole-2-thiones *IIa—IIIf* (Scheme 1). Efficiency of this photochemical isomerization was strongly dependent not only on the character of the substituent in position 2 but also on the presence of oxygen in the reaction mixture and energy of applied radiation. It follows (Table 1) that only in the case of benzyl (*Ia*) and diphenylmethyl (*Ib*) derivatives the corresponding thioketones *IIa* and *IIb* were formed in relatively high yields. Photolysis of *Ic—If* contrary to *Ia* and *Ib* led to predominant formation of *III*, while *IIc—IIIf* were formed in lower yields.

To explain comprehensive photoreactivity of studied thioethers *Ia—If* we performed also the photolysis of possible formed thioketones *IIa—IIIf* at λ_{irr}

Table 1. Composition of Reaction Mixtures after Photolysis of 2-Alkylthiobenzothiazoles in Dependence on Reaction Conditions

Compound	λ_{irr} nm	Reaction medium	t_{irr} min	Conv./% of Ia—Ij	Yield/% of IIa—IIj	Yield/% of III	Yield/% of IV	Yield/% of Va—Vf	Other products
Ia	> 290	Methanol	180	87	43	22	4	10	—
	> 290	Benzene	180	100	49	10	15	14	—
	> 290	n-Heptane	180	82	36	10	6	9	—
	253.7	Methanol	40	100	41	24	17	22	—
	> 290	Acetone	180	88	2.5	54	—	31	—
Ib	> 290	Methanol	180	91	43	19	—	—	—
	> 290	Benzene	180	86	61	9	—	—	—
	> 290	n-Heptane	180	81	59	12	14	—	—
	253.7	Methanol	30	88	32	44	13	—	—
	> 290	Acetone	180	87	27	30	—	—	—
Ic	> 290	Methanol	60	46	7	29	—	5	—
	> 290	Methanol	180	76	—	63	1	12	—
	> 290	Benzene	180	55	Traces	33	—	7	—
	> 290	n-Heptane	180	60	Traces	21	—	5	Derivatives and isomers of heptane (20 %)
	> 290	Acetone	180	100	—	49	—	12	—
Id	> 290	Methanol	360	12	2	7	< 1	—	—
	> 290	Methanol	600	59	7	40	2	9	—
	> 290	Benzene	600	67	2	44	2	13	—
	> 290	n-Heptane	600	78	2	1	1	5	Derivatives and isomers of heptane (55 %)
	> 290	Acetone	180	73	1	22	2	7	Methyl levulate (8 %) 2-Benzothiazolyacetic acid (6 %)
Ie	> 290	Methanol	60	99	16	47	13	10	—
	> 290	Benzene	20	96	19	71	—	13	—
	> 290	n-Heptane	30	94	12	37	5	15	—
	253.7	Methanol	20	83	15	44	19	1	—
	> 290	Acetone	30	93	17	67	—	8	—
If	> 290	Methanol	30	100	16	62	—	19	—
	> 290	Benzene	20	91	13	44	17	21	—
	> 290	n-Heptane	50	96	18	46	12	23	—
	253.7	Methanol	20	80	15	38	20	8	—
	> 290	Acetone	30	60	8	39	—	7	—

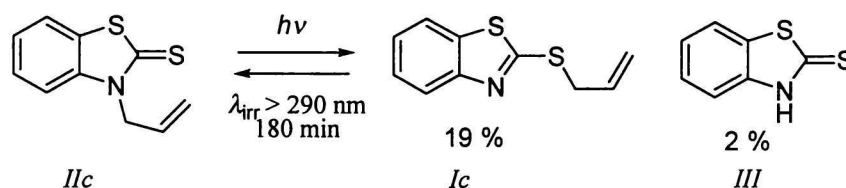
> 290 nm in the absence of oxygen. From these results it follows that all studied thioketones with the exception of allyl derivative *Iic* were photostable under the given reaction conditions. Photolysis of thioketone *Iic* led to the formation of thioether *Ic* and thioketone *III* (Scheme 2). On the basis of these results we can conclude that only photoisomerization of 2-allylthiobenzothiazole (*Ic*) under the formation of thioketone *Iic* is reversible.

The polarity of reaction medium does not have a significant effect on the photoreactivity of *Ia—If* but small increase in amounts of thioketone *III* after the

photolysis in methanol (unlike in the experiments in heptane and benzene) was observed (Table 1).

Irradiations of *Ia—If* at $\lambda_{irr} = 253.7$ nm caused the shortening of irradiation times in comparison with the irradiations at $\lambda_{irr} > 290$ nm. The main reason for this shortening was probably a higher energy of the used radiation and higher extinction coefficients of studied thioethers at $\lambda_{irr} = 253.7$ nm in comparison with $\lambda_{irr} > 290$ nm.

Characteristic feature of the photolysis of *Ia—If* with $\lambda_{irr} = 253.7$ nm was also the decrease of the yield of formed *III* with simultaneous increase of the



Scheme 2

yield of benzothiazole (IV). In the case of benzyl (Ia) and diphenylmethyl derivatives (Ib) a lowering of the yield of corresponding IIa and IIb was also observed. An increase of the yield of IV after photolysis of studied thioethers Ia–If with $\lambda_{irr} = 253.7$ nm was caused probably either by a higher participation of photocleavage of the benzothiazole–sulfur bond or by subsequent photodegradation of thioketone III (Scheme 1). The similar photodegradation of III especially in the presence of oxygen under the formation of IV was observed [11, 12].

To explain the photoreactivity of the studied 2-alkylthiobenzothiazoles Ia–If from their triplet states we performed also the sensitized photolysis with acetone ($\lambda_{irr} > 290$ nm) which was used as the sensitizer as well as the solvent. Under these conditions III was formed in higher yields than corresponding IIa–IIf (Table 1). For example, by photolysis of benzyl derivative Ia only traces of IIa were identified.

The most reactive of 2-alkylthiobenzothiazoles under sensitized conditions were naphthylmethyl derivatives Ie and If. This fact is connected probably with the possibility of energy transfer from excited triplet of acetone not only to benzothiazole skeleton of Ie and If but also to naphthalene moiety.

On the basis of presented results in Table 1 we assume that only T_1 state of benzyl derivative Ia leads to the predominant formation of thioketone III, while the photochemical reaction of the energetically richer S_1 state generates probably 3-benzyl-3H-benzothiazole-2-thione (IIa) as well as thioketone III. Formation of the above-mentioned thioketone III in direct photolysis is probably a consequence of the reactivity of T_1 state of Ia which is formed by the intersystem crossing (ISC) from S_1 state of Ia.

It is possible to suggest several mechanisms for the photochemical isomerization of 2-alkylthiobenzothiazoles to 3-alkyl-3H-benzothiazole-2-thiones. A reversible photoisomerization of Ic is probably realized as concerted Cope-type rearrangement. Such a type of mechanism has been also observed in the case of thermal reactivity of thioether Ic or 2-allyloxythiazole [13].

Photoisomerization of the other studied derivatives takes place probably either through concerted 1,3-shift of alkyl group or through a recombination of formed radical pairs. A decrease of efficiency of photoisomerization after sensitization with acetone is then in accord with knowledge that recombination of triplet radical pairs is not possible [14] and that triplet sensitization usually does not enable sigmatropic 1,3-shift of alkyl groups [15].

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