A STUDY OF PHOTOCYCLIZATION OF O-ALKYL N-(3-CHLORO-2-BENZO[*b*]THIENOCARBONYL)-MONOTHIOCARBAMATES

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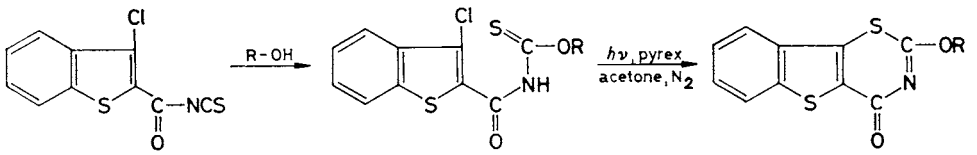
The O-alkyl N-(3-chloro-2-benzo[*b*]thienocarbonyl)monothiocarbamates prepared by the reaction of 2-isothiocyanatocarbonyl-3-chlorobenzo[*b*]thiophene with methanol, ethanol, 1-propanol, and 2-propanol are cyclized on irradiation with light of the wavelength above 300 nm to give high yields (80–90%) of 2-alkoxy-4*H*-benzo[*b*]thieno[2,3-*e*]-1,3-thiazin-4-one derivatives. From the absorption and emission spectra of the starting compounds as well as from a study of model compounds and influence of the reaction conditions it is presumed that the investigated intramolecular photosubstitution of chlorine by sulphur proceeds from the first singlet excited state (π, π^*) by a radical mechanism through the phase of radical complex formation.

Substitution reactions of aryl halides represent an important method of synthesis of organic compounds. Due to low reactivity of the starting substrates, the reaction usually only proceeds, if the carbon—halogen bond is weakened. For this purpose most frequently used are the catalysis by copper salts[1–3] or excitation of the substrate molecule by ultraviolet radiation[4–6]. In the photochemical reaction the reactivity decreases in the order: iodo > bromo > chloro derivatives, which corresponds to the increasing carbon–halogen bond energy. Recent trends prefer the use of chloro derivatives because of their greatest synthetical accessibility. In spite of considerable number of reports dealing with photocyclization reactions of aryl halides, only little attention has been paid to intramolecular substitution of halogen by sulphur. Only recently a preparation has been described of benzothiazine derivatives by intramolecular photocyclization of *o*-iodobenzoylthioamides[7], whereas, on the other hand, intermolecular photosubstituions of aryl halides with sulphur nucleophiles (proceeding by the $S_{RN}1$ mechanism) have been studied relatively well[8–10].

In our previous report[11] it is stated that N-(3-chloro-2-benzo[*b*]thienocarbonyl)--N′,N′-disubstituted thioureas are not cyclized thermally, in basic media, and/or with catalysis by copper salts, but an effective cyclization to benzothienothiazine proceeds photochemically. In continuation to this finding we studied photoreactivity of analogous N′-monosubstituted thioureas[12] and also that of the corresponding O-alkyl monothiocarbamates, which is to be reported in the present communication. In this study we were interested in the scope and limitations of this new photocycliza-

tion and especially in the effect of substitution of amino- by alkoxyresidue on the reactivity of the sulphur atom during the intramolecular photosubstitution of 3--chlorine in benzo[*b*]thiophene nucleus.

The starting O-alkyl N-(3-chloro-2-benzo[*b*]thienocarbonyl)monothiocarbamates (*I*) were prepared by addition of methanol, ethanol, 1- or 2-propanol to 2-isothiocyanatocarbonyl-3-chlorobenzo[*b*]thiophene (Scheme 1). UV spectra of the esters *I* exhibit strong absorption bands ($\log \varepsilon \sim 3$) at $\lambda_{max} \sim 310$ nm. Therefore, the photolysis was realized by action of the radiation of a high-pressure mercury discharge lamp using a pyrex filter transmitting the light of $\lambda > 300$ nm. The reaction gave high yields (80–90% of the isolated product) of 2-alkoxy-4*H*-benzo[*b*]thieno[2,3-*e*]--1,3-thiazin-4-ones (*II*). Methanol or acetone were used as the solvents, the latter being more advantageous with regard to solubility of the starting compounds. The high yields of the photocyclization products *II* as well as the relatively short time of irradiation indicate preparative importance of the reaction studied for the monothiocarbamate esters too, the reactivity of the latter compounds being comparable with that of the analogous N',N'-disubstituted thioureas[11].



I *II*

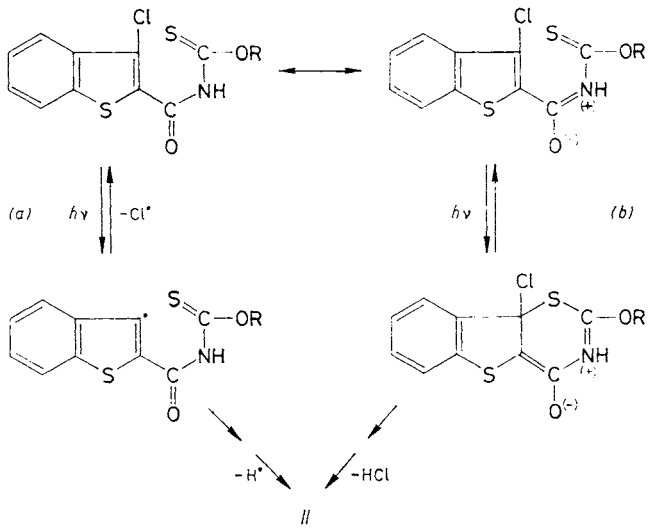
In formulae *I* and *II*: *a*, R = CH_3; *b*, R = CH_2CH_3; *c*, R = $CH_2CH_2CH_3$; *d*, R = $CH(CH_3)_2$

SCHEME 1

Structure of the compounds synthetized was confirmed by spectral methods. The IR absorption spectra of the benzothienothiazine *II* do not show absorption bands of NH groups which are found at 3 370 cm^{-1} in the spectra of esters *I*. Instead there appear characteristic bands of valence vibrations ν(C=N) at 1 560 cm^{-1}. Due to conjugation of carbonyl group with endocyclic C=N bond, the ν(C=O) bands found with the benzothienothiazines *II* at 1 640–1 650 cm^{-1} are shifted by about 40 cm^{-1} to lower wavenumbers as compared with the esters *I* whose ν(C=O) = = 1 680–1 690 cm^{-1}. The ^{1}H NMR spectra of esters *I* show resonance signals of the NH protons at $\delta = 10$ ppm, whereas these signals are absent from the spectra of the photocyclization products. The ^{13}C NMR spectra of the benzothienothiazines *II* lack the signal of thiocarbonyl carbon which is found – with the esters *I* – in the region of $\delta = 185$ ppm. Instead there is a signal of carbon of C=N double bond

at 165 ppm. The structure of benzothienothiazines is unambiguously confirmed also by the mass spectrum of compound *IIa* in which the main path of splitting of the molecular ion is connected with splitting off of the $NCOCH_3$ fragment.

Two mechanisms, *viz.* a radical (*a*) and an electrocyclic (*b*) one (Scheme 2) can be presumed for the photocyclization of monothiocarbamate esters *I* giving benzothienothiazines *II*. The radical course starts with C—Cl bond homolysis followed by a six-



SCHEME 2

-membered ring closure. In the other case (*b*) the reaction involves a mesomeric form with conjugated system of six π electrons similar to the enamide cyclization[5,13,14]. In the excited state the six-membered ring is formed, and in a subsequent step hydrogen chloride is split off thermally.

According to the ideas predominating in the past the photocyclizations involving 6π electron systems with a halogen on the carbon atom on which the bond is formed proceed *via* an electrocylic conrotational process[5,15–18]. More recent works based on detailed investigations of the mechanism and study of energetics of the excited state, reactivity of model compounds, effect of reaction conditions on the reaction course, and identification of the intermediates by the flash photolysis method showed unambiguously[19–23] that the reaction type discussed proceeds by a radical mechanism. In the cases in which the energy of the reaction excited state was lower than the dissociation energy of carbon–halogen bond it was impossible to prove the presence of a reduction product (substitution of the halogen by hydrogen) in the reaction mixture, which contradicts the C—Cl bond homolysis giving free radicals. For these cases the so-called radical complexation mechanism was suggested[19–23]. The energy deficit of the excited state is here compensated by the energy released from the simultaneous formation of the new bond. The radical complex formed (*A*, Scheme 5) splits off the halogen radical and, in the subsequent step, hydrogen radical is split off to give hydrogen halide and the stable final product.

In our case the most likely reaction excited state is the first singlet excited state S_1 formed by an excitation in the region of 310 nm, because the reaction time and yield of the product are the same in the presence of molecular oxygen as in nitrogen atmosphere (*cf. e.g.* refs[23,24]). If the triplet state were operating, the presence of oxygen would substantially affect the reaction course (see *e.g.* ref.[25]) due to the triplet state being efficiently quenched by molecular oxygen.

The character of the excited state S_1 was studied with ester *Ia* using the emission and absorption electronic spectra. The investigation of emission spectra of compound *Ia* (the exciting light of $\lambda = 313$ nm) in methanol, poly(methyl methacrylate) or poly(styrene) film (concentration 5% by weight) showed that the compound exhibits no measurable fluorescence at room temperature in the apparatus used[26,27]. At the temperature of 77 K intensive green phosphorescence was observed at $\lambda_{max} = 540$ nm with a shoulder at 520 nm. The energy of the first triplet state calculated from the value 520 nm is relatively low, $E(T_1) = 230$ kJ mol^{-1}. As the ester *Ia* shows no fluorescence, the position of O—O transition needed for calculation of energy of the S_1 state was assessed from the slightly distinct vibrational structure of the absorption band in heptane at room temperature (Fig. 1). According to the position of the shoulder at 345 nm (denoted by an arrow) the approximate energy value of the first singlet excited state is $E(S_1) = 346$ kJ mol^{-1}. Applicability of the absorption spectra measured at room temperature to the assessment of $E(S_1)$ is reported in refs[28-30]. The $E(S_1)$ and $E(T_1)$ values found enable determination of singlet-triplet splitting $\Delta E(ST) = 116$ kJ mol^{-1}. This value is relatively large, which is typical for (π,π^*) states in contrast to the (n, π^*) states, where $\Delta E(ST)$ usually is below 60 kJ mol^{-1} (ref.[31]). The high value of singlet-triplet splitting ($\Delta E(ST)$), the shifts of the long-wave maximum to shorter-wave region on going to non-polar solvents ($\lambda_{max} = 310$ nm in ethanol, 308 nm in dioxane, 306 nm in cyclohexane, and 305 nm in heptane), and the intensive absorption ($\log \varepsilon \sim 3$) indicate the (π, π^*) character of the S_1 state.

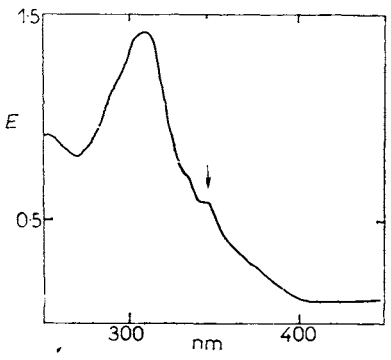
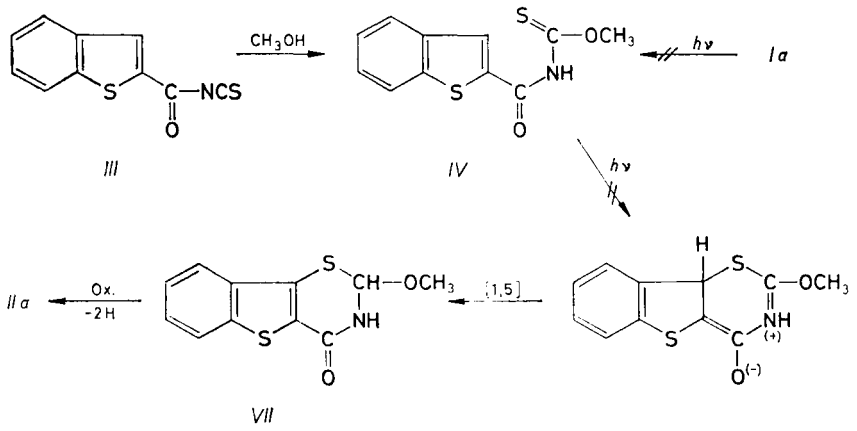


FIG. 1

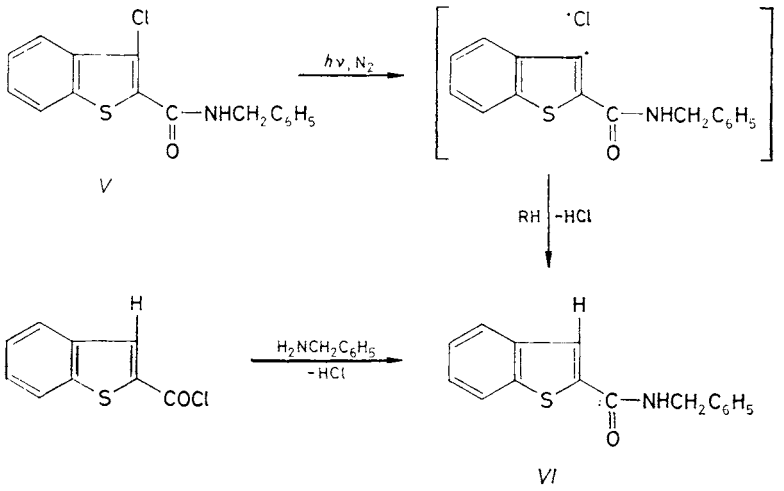
Absorption spectrum of methyl ester *Ia* in heptane; $c = 1 \cdot 10^{-5}$ mol l^{-1}

The assessed value $E(S_1) = 346\ \text{kJ mol}^{-1}$ is lower than the C_{Ar}—Cl bond dissociation energy (397 kJ mol^{-1}, ref.[32]), hence it is insufficient for the C—Cl bond homolysis giving free radicals from esters *I*. If such radicals were formed, their reaction with solvent (as a hydrogen donor) would produce the reduction products containing hydrogen atom instead of chlorine at 3-position of the benzo[*b*]thiophene skeleton. The absence of the reduced ester was unambiguously confirmed in the case of compound *Ia* by TLC comparison of the raw reaction mixture (after irradiation) with the standard O-methyl N-(2-benzo[*b*]thienocarbonyl)monothiocarbamate (*IV*) prepared by addition of methanol to 2-isothiocyanatocarbonylbenzo[*b*]thiophene (*III*, Scheme 3). The presence of compound *IV* could not be proved even by increasing of its concentration, irradiation through quartz and/or application of cyclohexane or 2-propanol as the solvents which are known to readily supply the hydrogen atom in reactions with radicals[33]. The formation of radicals by C—Cl bond homolysis during photolysis of analogous derivatives of 3-chlorobenzo[*b*]thiophene with sufficient energy of the excited state, *i.e.* with the efficient absorption at $\lambda < 300$ nm



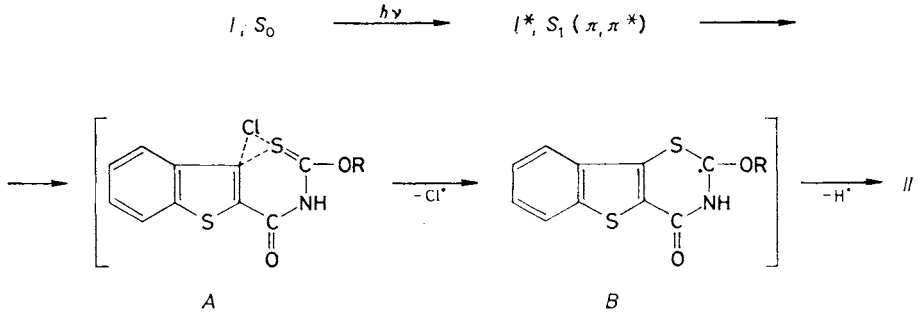
SCHEME 3

(ref.[20]), was confirmed by irradiation of N-benzylamide of 3-chlorobenzo[*b*]thiophene-2-carboxylic acid (*V*, $\lambda_{max} = 287$ nm) prepared by the reaction of benzylamine with 3-chlorobenzo[*b*]thiophene-2-carbonyl chloride. The photolysis of compound *V* in acetone (which solvent can also act as hydrogen donor in photoreductions of aryl halides[34]) irradiated through quartz gave a 34% yield of the corresponding reduced product, N-benzylamide of benzo[*b*]thiophene-2-carboxylic acid (*VI*, Scheme 4). The reaction yield was increased to 47% and the reaction time was reduced to one third by replacement of the acetone solvent by a 1 : 1 mixture of acetone and 2-propanol. Structure of the product *VI* was confirmed by independent synthesis from benzylamine and benzo[*b*]thiophene-2-carbonyl chloride.



SCHEME 4

Investigation of the photoreactivity of ester *IV* gave the results enabling exclusion of the presumption of operation of the electrocyclic mechanism. The electrocyclic reaction should be connected with photocyclization of compound *IV* to benzothienothiazine *IIa* and/or its reduced form (*VII*, Scheme 3). However, irradiation of compound *IV* (λ_{max} = 312 nm) through the pyrex filter in acetone, methanol, or acetonitrile causes no cyclization reaction, no change of the starting compound being observed even after 10 h with bubbling through nitrogen or air. From this finding, in the sense of published data[19–22], it follows that the cyclization of 3-chloro derivative *Ia* does not proceed electrocyclically either. Even if the ester *IV* were cyclized to the benzothienothiazine *IIa*, the electrocyclic photocyclization mechanism of 3-chloro derivatives *I* would be less likely than the radical mechanism, since the radical intermediate type *B* (Scheme 5) was identified by the flash photolysis method in analogous systems[23].



SCHEME 5

From the results obtained it follows that the reaction studied by us proceeds neither *via* free radicals nor electrocyclically. Hence it can be presumed that the photocyclization of esters *I* to benzothienothiazines *II* goes by the radical mechanism through a phase of radical complexation (Scheme 5). The radical complex *A* is probably easily formed due to high polarizability of sulphur atom. In the subsequent step chlorine radical is split off to give the radical intermediate *B* which is extensively stabilized by free electron pairs of the adjacent heteroatoms[35-37]. In the last step, hydrogen radical is split off with formation of HCl and the photocyclization product *II*.

EXPERIMENTAL

The infrared spectra were measured in chloroform with an IR-75 apparatus (Zeiss Jena), the wavenumber values are given in cm^{-1}. The ^1H and ^{13}C NMR spectra were measured in deuteriochloroform using a Tesla BS 487 A (80 MHz) and a Tesla BS 567 (25·15 MHz) apparatus, respectively, with tetramethylsilane as the internal standard. The δ values are given in ppm. The UV spectra were measured with a Perkin–Elmer 402 apparatus in ethanol, and the emission spectra were measured with the apparatus described in refs[26,27]. The positions of absorption and emission maxima are given in nm. The mass spectrum of compound *IIa* was recorded with an LKB 9000 apparatus at the ionisation energy of 70 eV at the temperature of the ionisation chamber 240°C.

The photochemical reactions were carried out with the use of a high-pressure mercury discharge lamp TQ 150 (Original Hanau) in an immersion apparatus equipped with a magnetic stirrer with the radiator placed in a quartz water-cooled casing. The reaction course was followed by thin layer chromatography using the Silufol plates (Kavalier).

3-Chloro-2-chlorocarbonylbenzo[*b*]thiophene[38], 3-chloro-2-isothiocyanatocarbonylbenzo[*b*]-thiophene[11], and 2-chlorocarbonylbenzo[*b*]thiophene[39] were prepared according to the literature.

O-Alkyl N-(3-Chloro-2-benzo[*b*]thienocarbonyl)monothiocarbamates (*I*)

A solution obtained from 3 g (13 mmol) 3-chloro-2-isothiocyanatocarbonylbenzo[*b*]thiophene and 300–350 ml warm methanol (ethanol, 1- or 2-propanol) was refluxed 40 min, whereupon 800 ml warm water was added slowly, and the mixture was left to attain room temperature. The separated crystalline product was collected by suction and dried.

O-*Methyl* N-(3-*Chloro*-2-*benzo*[*b*]*thienocarbonyl*)*monothiocarbamate* (Ia). Yield 80%, m.p. 133–135°C. For $C_{11}H_8ClNO_2S_2$ (285·7) calculated: 46·24% C, 2·82% H, 4·90% N; found: 46·25% C, 2·92% H, 4·53% N. IR: 3 370 (N—H), 3 010 (C—H)$_{Ar}$, 2 950 $(CH_3)_{as}$, 1 680 (C=O), 1 500 (NHCS). ^1H NMR: 4·20 (s, 3 H, CH_3), 7·44, 7·85 (m, m, 4 H, C_6H_4), 10·15 (s, 1 H, NH). ^{13}C NMR: 59·35 (q, CH_3), 120·94, 122·81, 123·70, 125·87, 128·61, 131·39, 136·69, 138·86 (benzo[*b*]thiophene skeleton), 155·80 (s, C=O), 188·73 (s, C=S). UV, λ_{max} (log ε): 211 (3·18), 310 (3·06).

O-*Ethyl* N-(3-*Chloro*-2-*benzo*[*b*]*thienocarbonyl*)*monothiocarbamate* (Ib). Yield 85%, m.p. 108–109°C. For $C_{12}H_{10}ClNO_2S_2$ (299·7) calculated: 48·09% C, 3·36% H, 4·67% N; found: 47·83% C, 3·31% H, 4·70% N. IR: 3 355 (N—H), 3 010 (C—H)$_{Ar}$, 1 685 (C=O), 1 510 (NHCS). ^1H NMR: 1·67 (t, J = 3·5 Hz, 3 H, CH_3), 4·63 (q, J = 3·5 Hz, 2 H, CH_2), 7·45, 7·78 (m, m, 4 H, C_6H_4), 10·03 (s, 1 H, NH). ^{13}C NMR: 13·74 (q, CH_3), 69·43 (t, CH_2), 120·87, 122·81,

123·63, 125·79, 128·33, 131·47, 136·69, 138·78 (benzo[*b*]thiophene skeleton), 155·65 (s, C=O), 187·98 (s, C=S). UV, λ_{max} (log ε): 211 (3·16), 307 (3·07).

O-*Propyl* N-(3-*Chloro*-2-*benzo*[*b*]*thienocarbonyl*)*monothiocarbamate* (Ic). Yield 84%, m.p. 106·5–107°C. For $C_{13}H_{12}ClNO_2S_2$ (313·7) calculated: 49·78% C, 3·85% H, 4·47% N; found: 49·81% C, 3·98% H, 4·46% N. IR: 3 375 (N—H), 3 000 $(C—H)_{Ar}$, 1 680 (C=O), 1 510 (NHCS). ^{1}H NMR: 1·05 (t, J = 3·5 Hz, 3 H, CH_3), 1·83 (m, 2 H, CH_2), 4·05 (t, J = 3·5 Hz, 2 H, OCH_2), 7·48, 7·83 (m, m, 4 H, C_6H_4), 10·08 (s, 1 H, NH). ^{13}C NMR: 10·38 (q, CH_3), 21·65 (t, CH_2), 75·18 (t, OCH_2), 120·87, 122·81, 123·63, 125·79, 128·33, 131·47, 136·62, 138·71 (benzo[*b*]thiophene skeleton), 155·51 (s, C=O), 188·29 (s, C=S). UV, λ_{max} (log ε): 213 (3·10), 307 (3·03).

O-*Isopropyl* N-(3-*Chloro*-2-*benzo*[*b*]*thienocarbonyl*)*monothiocarbamate* (Id). Yield 91%, m.p. 90–92°C. For $C_{13}H_{12}ClNO_2S_2$ (313·7) calculated: 49·78% C, 3·85% H, 4·47% N; found: 49·86% C, 4·27% H, 4·31% N. IR: 3 365 (N—H), 3 005 $(C—H)_{Ar}$, 1 690 (C=O), 1 510 (NHCS). ^{1}H NMR: 1·45 (d, J = 6 Hz, 6 H, $(CH_3)_2$), 5·61 (m, 1 H, CH), 7·45, 7·80 (m, m, 4 H, C_6H_4), 9·98 (s, 1 H, NH). ^{13}C NMR: 21·20 (q, CH_3), 78·01 (d, CH), 120·79, 122·81, 123·63, 125·79, 128·33, 131·54, 136·69, 138·71 (benzo[*b*]thiophene skeleton). UV, λ_{max} (log ε): 211 (3·12), 305 (3·04).

2-Alkoxy-4*H*-benzo[*b*]thieno[2,3-*e*]-1,3-thiazin-4-ones (*II*)

A solution of 3·5 mmol ester *I* in 250 ml acetone was irradiated through a pyrex filter for 30 (*Ia*), 50 (*Ib*), 60 (*Ic*), or 50 (*Id*) min. Nitrogen gas was bubbled through the solution 15 min before the irradiation and during the reaction. When the starting compound was consumed, the solvent was evaporated, and the residue was dissolved in 5–10 ml chloroform and submitted to chromatography on a column of 100 g silica gel (100–250 μm) using benzene–acetone mixture (7 : 1) as the eluent. The product was recrystallized from methanol.

2-*Methoxy*-4*H*-*benzo*[*b*]*thieno*[2,3-*e*]-1,3-*thiazin*-4-*one* (IIa). Yield 81%, m.p. 181–183°C. For $C_{11}H_7NO_2S_2$ (249·3) calculated: 52·95% C, 2·83% H, 5·62% N; found: 52·71% C, 2·63% H, 5·29% N. Mass spectrum (*m/z*; relative intensity, %): 249 (46), $[M^{\cdot+}]$, 192 (100), $[M - NCOCH_3]^+$. IR: 3 015 $(C—H)_{Ar}$, 2 955 $(CH_3)_{as}$, 1 650 (C=O), 1 570 (C=N). ^{1}H NMR: 4·20 (s, 3 H, CH_3), 7·60 (m, 4 H, C_6H_4). ^{13}C NMR: 57·78 (q, CH_3), 122·43, 123·64, 125·42, 126·69, 128·93, 131·02, 125·20, 141·55 (benzo[*b*]thiophene skeleton), 165·73 (s, C=N), 171·56 (s, C=O). UV, λ_{max} (log ε): 215 (3·01), 255 (2·88,) 305 (2·83).

2-*Ethoxy*-4*H*-*benzo*[*b*]*thieno*[2,3-*e*]-1,3-*thiazin*-4-*one* (IIb). Yield 92%, m.p. 170–172°C. For $C_{12}H_9NO_2S_2$ (263·3) calculated: 54·74% C, 3·44% H, 5·32% N; found: 54·58% C, 3·68% H, 5·60% N. IR: 3 010 $(C—H)_{Ar}$, 1 645 (C=O), 1 570 (C=N). ^{1}H NMR: 1·47 (t, J = 3·5 Hz, 3 H, CH_3), 4·70 (q, J = 3·5 Hz, 2 H, CH_2), 7·60 (m, 4 H, C_6H_4). ^{13}C NMR: 14·18 (q, CH_3), 67·56 (t, CH_2), 122·43, 123·55, 125·35, 126·54, 128·93, 131·24, 135·20, 141·40 (benzo[*b*]thiophene skeleton), 165·96 (s, C=N), 171·03 (s, C=O). UV, λ_{max} (log ε): 215 (3·05), 255 (2·19), 305 (2·87).

2-*Propoxy*-4*H*-*benzo*[*b*]*thieno*[2,3-*e*]-1,3-*thiazin*-4-*one* (IIc). Yield 94%, m.p. 195–196·5°C. For $C_{13}H_{11}NO_2S_2$ (277·4) calculated: 56·29% C, 3·99% H, 5·05% N; found: 56·40% C, 4·06% H, 4·97% N. IR: 3 010 $(C—H)_{Ar}$, 1 640 (C=O), 1 560 (C=N). ^{1}H NMR: 1·03 (t, J = 3·5 Hz, 3 H, CH_3), 1·88 (m, 2 H, CH_2), 4·58 (t, J = 3·5 Hz, 2 H, OCH_2), 7·62 (m, C_6H_4). ^{13}C NMR: 10·23 (q, CH_3), 21·87 (t, CH_2), 73·09 (t, OCH_2), 122·51, 123·70, 125·42, 126·58, 128·93, 131·24, 135·27, 141·55 (benzo[*b*]thiophene skeleton), 166·03 (s, C=N), 171·33 (s, C=O). UV, λ_{max} (log ε): 216 (3·07), 250 (2·96), 304 (2·80).

2-*Isopropoxy*-4*H*-*benzo*[*b*]*thieno*[2,3-*e*]-1,3-*thiazin*-4-*one* (IId). Yield 87%, m.p. 158–160°C. For $C_{13}H_{11}NO_2S_2$ (277·4) calculated: 56·29% C, 3·99% H, 5·05% N; found: 56·32% C, 4·10% H,

4·93% N. IR: 3 010 $(C—H)_{Ar}$, 1 640 (C=O), 1 565 (C=N). ^1H NMR: 1·45 (d, $J = 6$ Hz, 6 H, $(CH_3)_2$), 5·75 (m, 1 H, CH), 7·60 (m, 4 H, C_6H_4). ^{13}C NMR: 21·72 (q, CH_3), 75·85 (d, CH), 122·51, 123·70, 125·35, 126·54, 128·93, 131·54, 135·35, 141·40 (benzo[*b*]thiophene skeleton), 166·18 (s, C=N), 170·81 (s, C=O). UV, λ_{max} (log ε): 215 (3·10), 252 (2·89), 303 (3·01).

Oxidative Photolysis of O-Methyl N-(3-Chloro-2-benzo[*b*]thienocarbonyl)-monothiocarbamate (*Ia*)

A solution of 1 g (3·5 mmol) ester *Ia* in 250 ml acetone was irradiated through a pyrex filter while bubbling through air for 30 min. The acetone was evaporated, the residue was dissolved in 10 ml chloroform and purified by column chromatography (100 g silica gel 100—250 μm; benzene–acetone 7 : 1) to give 0·7 g (81%) benzothienothiazine *IIa*.

2-Isothiocyanatocarbonylbenzo[*b*]thiophene (*III*)

A solution of 3 g (15 mmol) 2-chlorocarbonylbenzo[*b*]thiophene in 50 ml anhydrous benzene was treated with 3·7 g (11·4 mmol) lead(II) thiocyanate, and the mixture was refluxed with stirring 2·5 h. The warm mixture was filtered with charcoal, and the solvent was evaporated. The residue was recrystallized from petroleum ether. Yield 2·7 g (80%), m.p. 47—49°C. For $C_{10}H_5NOS_2$ (219·3) calculated: 54·78% C, 2·30% H, 6·39% N; found: 54·62% C, 2·41% H, 6·45% N. IR: 1 960 $(N=C=S)_{as}$, 1 680 (C=O). ^1H NMR: 7·45, 7·85 (m, m, 4 H, C_6H_4), 8·10 (s, 1 H, H_3).

O-Methyl N-(2-Benzo[*b*]thienocarbonyl)monothiocarbamate (*IV*)

A solution of 1·4 g (6·4 mmol) isothiocyanate *III* in 350 ml methanol was refluxed 40 min, the methanol was evaporated, and the evaporation residue was recrystallized from a benzene–petroleum ether mixture. Yield 1·3 g (81%), m.p. 119—121°C. For $C_{11}H_9NO_2S_2$ (251·3) calculated: 52·57% C, 3·61% H, 5·57% N; found: 52·31% C, 3·46% H, 5·67% N. IR: 3 400 (N—H), 3 020 $(C—H)_{Ar}$, 1 695 (C=O), 1 480 (NHCS). ^1H NMR: 4·15 (s, 3 H, CH_3), 7·33, 7·80 (m, m, 4 H, C_6H_4), 7·82 (s, 1 H, H_3), 9·35 (s, 1 H, NH). ^{13}C NMR: 59·90 (q, CH_3), 122·73, 125·35, 125·79, 127·44, 127·66, 136·92, 138·71, 142·14 (benzo[*b*]thiophene skeleton), 157·52 (s, C=O), 189·40 (s, C=S). UV, λ_{max} (log ε): 211 (3·11), 312 (3·13).

N-Benzylamide of 3-Chlorobenzo[*b*]thiophene-2-carboxylic Acid (*V*)

A solution of 3 g (16 mmol) 3-chloro-2-chlorocarbonylbenzo[*b*]thiophene in 150 ml acetone was treated with 3·4 g (32 mmol) benzylamine and stirred at room temperature 2 h. The separated white solid (benzylammonium chloride) was collected by suction, the filtrate was concentrated to one half of its original volume, whereupon 200 ml water was added thereto. The separated solid was collected by suction, dried, and recrystallized from ethanol. Yield 3·2 g (68%), m.p. 119—121°C. For $C_{16}H_{12}ClNOS$ (301·3) calculated: 63·68% C, 4·01% H, 4·64% N; found: 63·50% C, 4·12% H, 4·82% N. IR: 3 430 (N—H), 3 020 $(C—H)_{Ar}$, 1 645 (C=O). ^1H NMR: 4·70 (d, $J = 2·5$ Hz, 2 H, CH_2), 7·35, 7·75 (m, m, 4 H, 5 H, C_6H_4, C_6H_5). UV (CH_3OH), λ_{max} (log ε): 211 (3·14), 237 (3·03), 287 (2·89).

N-Benzylamide of Benzo[*b*]thiophene-2-carboxylic Acid (*VI*)

A. A solution of 0·9 g (3 mmol) amide *V* in 250 ml acetone was irradiated through quartz 27 h, while nitrogen gas was bubbled through. The acetone was evaporated, the evaporation

residue was dissolved in 5 ml chloroform and purified by column chromatography (100 g silica gel 100–160 μm; benzene–acetone 19 : 1). Yield 0·27 g (34%).

B. A solution of 0·9 g (3 mmol) amide *V* in a mixture of 125 ml acetone and 125 ml 2-propanol was irradiated 9 h, and the mixture was treated further in the same way as *sub A*. Yield 0·38 g (47%).

C. Starting from 0·5 g (2·5 mmol) 2-chlorocarbonylbenzo[*b*]thiophene and 0·54 g (5 mmol) benzylamine in 50 ml acetone, the product *VI* was obtained in the same way as the compound *V* above. Yield 0·46 g (70%). M.p. 144–145°C (ethanol). For $C_{16}H_{13}NOS$ (267·4) calculated: 71·97% C, 4·94% H, 5·24% N; found: 72·09% C, 4·80% H, 5·38% N. IR: 3 420 (N—H), 3 000 $(C—H)_{Ar}$, 1 630 (C=O). ^1H NMR: 4·55 (d, J = 2·5 Hz, 2 H, CH_2), 7·31, 7·85 (m, m, 4 H, 5 H, C_6H_4, C_6H_5), 7·93 (s, 1 H, H_3), 8·50 (t, J = 2·5 Hz, 1 H, NH).

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