

128. Photochemistry of Isothiocoumarin (= 1*H*-[2]Benzothiopyran-1-one)

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Irradiation ($\lambda = 350$ nm) of 1*H*-[2]benzothiopyran-1-one (**2**) in the solid state affords selectively and in good yield 6 α ,6 β ,12 β ,12 α -tetrahydrocyclobuta[1,2-*c*:4,3-*c'*]bis([2]benzothiopyran)-5,8-dione (**3**), the head-to-head (*HH*) *cis-cisoid-cis*-cycloclodimer of **2**. X-Ray analysis of **2** confirms that this reaction proceeds according to the well-established topochemical principles. The same dimer **3** is obtained in low yields on irradiation of 10^{-1} M solutions of **2** in either MeOH or MeCN, while no conversion at all is observed in benzene. On irradiation of **2** in MeCN in the presence of tetrachloroethene, the [2+2] photocycloadduct **4** is formed in good yield, the conversion **2** \rightarrow **4** being efficiently quenched by naphthalene. In contrast, no reaction is observed on irradiation of **2** in the presence of 2,3-dimethylbut-2-ene, neither in polar nor in apolar solvents.

Introduction. – Within the scope of our investigations on the photochemistry of (S-hetero)cyclic unsaturated carbonyl compounds [1], we had found that 2*H*-[1]benzothiopyran-2-one (**1**) undergoes photocyclodimerization efficiently, in solution [2] as well as in the solid state [3], and that both **1** itself and pyrano-, thiopyrano- and furo-fused thiocoumarins are converted quantitatively to mixtures of *cis*- and *trans*-fused [2+2] cycloadducts on irradiation in the presence of an excess of 2,3-dimethylbut-2-ene [4] [5].

In contrast to thiocoumarins, research on the isomeric isothiocoumarins and their derivatives has been almost totally neglected [6]. Here, we report results on the photochemical behavior of the parent compound 1*H*-[2]benzothiopyran-1-one (**2**).

Results. – On irradiation ($\lambda = 350$ nm) of 10^{-1} M solutions of **2** in different solvents (benzene, *i*-PrOH, MeCN, or MeOH), only very low degrees of conversion to a new product **3** are achieved, the highest yields of **3** (*Scheme*), as determined by ¹H-NMR analysis, being 17% in MeOH.

However, solid-state irradiation of **2** affords the same product **3** efficiently and in nearly quantitative yield. The assignment of the *HH-cis-cisoid-cis*-photocyclodimer structure to **3** stems from both X-ray analysis and ¹H-NMR spectroscopy (*Fig.*). To verify whether this reaction proceeds according to the well-established topochemical rules for bimolecular photoreactions in crystals [7], an X-ray analysis of **2** was also performed. Indeed, the distance between two (coplanar) molecules of **2** was found to be 4.036 Å.

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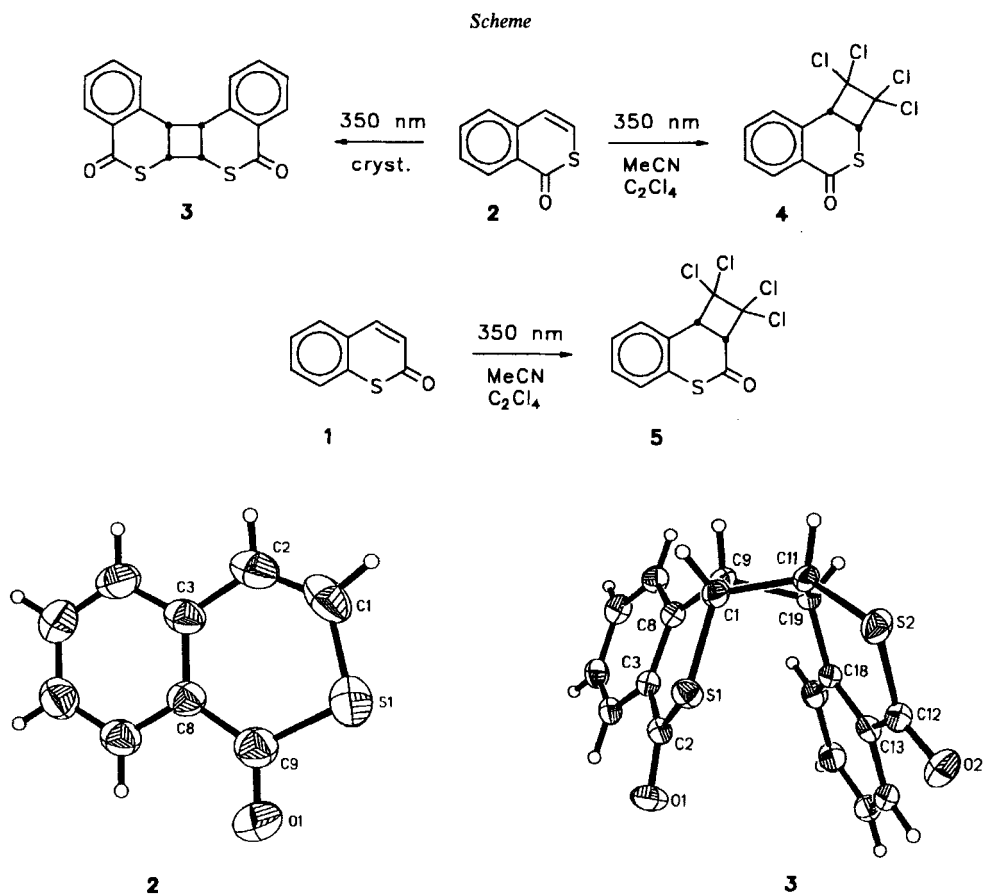


Fig. 1. X-Ray structures of compounds **2** and **3**

On irradiation of **2** in solution in the presence of 2,3-dimethylbut-2-ene, no product formation is observed, neither in MeCN nor in benzene as solvents. In contrast, irradiation of **2** in MeCN containing an excess of tetrachloroethene leads to the selective formation of the *cis*-fused [2+2] photocycloadduct **4**, obtained in 45% yield after separation and purification by chromatography. To assign the multiplicity of excited **2** in this reaction, a *Stern-Volmer* experiment was run. Indeed, the conversion $2 \rightarrow 4$ is efficiently diminished by adding increasing amounts of naphthalene as a (triplet) quencher. The resulting slope has a value of $k_q \cdot \tau \approx 90$ l/mol. Both **1** and **2** were irradiated in MeCN in the presence of tetrachloroethene in a merry-go-round setup in order to determine the relative rates of formation of the corresponding [2+2] cycloadducts **5** and **4**, respectively (*Scheme*). Thiocoumarin (**1**) reacts *ca.* five times faster than its isomer **2**.

Finally, in an additional experiment **1** was irradiated in MeCN in the presence of either tetrachloroethane or 2,3-dimethylbut-2-ene. The formation of [2+2] cycloadducts [**1**] with this latter alkene proceeds *ca.* 40 times faster than with tetrachloroethene.

Discussion. – Regarding the solid-state photodimerization experiment, the behavior of **2** parallels that of **1**, *i.e.*, the corresponding *HH-cis-cisoid-cis*-photocyclodimer is formed selectively. In such topochemical reactions, the proximity and degree of parallelism of the reacting centers are crucial for the dimerization, a maximum value of 4.2 Å for the separation of the two reactive double bonds having been proposed [8]. The experimental value obtained for **2** (4.036 Å) fits nicely to this rule, while for **1** no X-ray analysis has been reported so far.

On irradiation in solution, however, the two isomers **1** and **2** differ remarkably. The behavior of **1** is very similar to that of simple cyclic α,β -unsaturated ketones, *e.g.*, cyclohex-2-enone or cyclopent-2-enone, as it affords the *HH-cis-transoid-cis*-photocyclodimer preferentially, and it reacts so much more efficiently with alkenes the lower their ionization potential. The fact that **2** affords the same photocyclodimer **3** on irradiation in solution – albeit in very low yield – as in the solid suggests the formation of a pre-aligned complex, most probably an excimer, which results from π interaction between the aromatic rings of an excited- and a ground-state molecule of **2**. The difference in reactivity between (triplet) excited **2** vs. tetrachloroethene on the one hand and 2,3-dimethylbut-2-ene on the other is probably due to the higher polarizability of the former, as the two alkenes have almost identical triplet energies ($E_T \approx 330$ kJ) and differ in their ionization potential by less than 1 eV (tetrachloroethene: $I_p \approx 9.1$ eV, 2,3-dimethylbut-2-ene: $I_p \approx 8.3$ eV) [9]. All this suggests that the C-atoms of the C=C bond in (triplet)excited **2** – or at least one of them – have a much higher electron density than those in **1**. The minimum lifetime of triplet excited **2** in MeCN corresponds to $\tau \approx 3$ –4 ns, assuming a value of $k_q = 2.9 \cdot 10^{10}$ l/mol \cdot s [9].

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Experimental Part

General. The benzothiopyranones **1** [10] and **2** [11] were synthesized according to the literature procedures. Photolyses: *Rayonet RPR-100* photoreactor equipped with 350-nm lamps. GC: 30-m *SE 30* capillary column. ^1H - and ^{13}C -NMR Spectra: at 400 and 100.6 MHz, resp.; chemical shifts in ppm rel. to TMS (= 0 ppm), coupling constants J in Hz. X-Ray analyses: *Stoe-Siemens AED* four circle diffractometer at 293 K (for **2**), and *Enraf-Nonius-CAD-4* four circle diffractometer at 173 K (for **3**), both with CuK_α radiation ($\lambda = 1.54178$ Å).

X-Ray Analysis of 2. Prismatic, pale-yellow transparent blocks, $0.61 \times 0.46 \times 0.15$ mm, were obtained by recrystallization from pentane. M.p. 76°. Crystal data: $\text{C}_9\text{H}_6\text{OS}$, $M_r = 162.2$, orthorhombic, space groups $P2_12_12_1$, $a = 4.036(4)$, $b = 11.806(14)$, $c = 15.695(17)$ Å, $V = 747.8(1)$ Å³, $Z = 4$, $D_x = 1.441$ g \cdot cm⁻³, $F(000) = 336$, $\mu = 3.26$ mm⁻¹. The cell parameters were determined by least-squares refinement against the setting angles of 32 reflections, $\Phi = 30.2$ – 31.4° . Of the 681 independent reflections ($\Phi_{\text{max}} = 60.4^\circ$), 616 were considered to be observed [$I > 2\sigma(I)$]. Final R value for all reflections $R = 0.053$ ($\omega R2 = 0.1430$). *Flack* parameter = $0.02(7)^3$.

Solid-State Irradiation of 2. Solns. of 10 mg (0.062 mmol) of **2** in 1 ml of Et_2O in a 5-ml tapered flask are slowly evaporated to produce a homogeneous solid film. Four such flasks are then purged with Ar and irradiated for 7 h. Chromatography ($\text{SiO}_2/\text{CH}_2\text{Cl}_2$) affords 32 mg (83%) of *6aa,6ba,12ba12ca-tetrahydrocyclobuta[1,2-c:4,3-c']bis([2]benzothiopyran)-5,8-dione* (**3**). M.p. 214°. ^1H -NMR ((D_6)acetone): 7.77 (*d*, $J = 8.0$); 7.33 (*d*, $J = 7.5$); 7.26 (*t*, $J = 7.5$); 6.93 (*d*, $J = 8.0$); 5.09, 4.82 (*AA'XX'*, $J_{AA'} = 8.5$, $J_{AX} = 8.3$, $J_{AX'} = 1.5$, $J_{XX'} = -5.5$). ^{13}C -NMR ((D_6)acetone): 188.3 (*s*); 138.9 (*s*); 133.7 (*d*); 131.8 (*s*); 128.1 (*d*); 126.6 (*d*); 46.9 (*d*); 43.0 (*d*).

³⁾ Crystallographic data were deposited with the *Cambridge Crystallographic Data Center*, University Chemical Laboratory, 12 Union Road, Cambridge CB2 1EZ, England.

X-Ray Analysis of 3. Transparent blocks, $0.5 \times 0.4 \times 0.3$ mm, were obtained by recrystallization from acetone. M.p. 214° . Crystal data: $C_{18}H_{12}O_2S_2$, $M_r = 324.4$, monoclinic, space group $P2_1$, $a = 7.640(1)$, $b = 11.931(1)$, $c = 8.544(1)$ Å, $\beta = 114.86(1)$, $V = 706.6(2)$ Å³, $Z = 2$, $D_x = 1.525$ g · cm⁻³, $F(000) = 336$, $\mu = 3.446$ mm⁻¹. The cell parameters were determined by least-squares refinement against the setting angles of 25 reflections, $\Phi = 41.3$ – 44.5° . Of the 1555 independent reflections ($\Phi_{max} = 76.5^\circ$), 1546 were considered to be observed [$I > 2\sigma(I)$]. Final R value for all reflections $R = 0.04$ ($\omega R2 = 0.1083$). Flack parameter = $0.02(3)^3$.

Photolysis of 2 in Soln. Ar-degassed solns. of 10 mg (0.062 mmol) of **2** in 0.6 ml of MeOH, MeCN, i-PrOH, or benzene are irradiated for 50–60 h. After evaporation of the solvent, ¹H-NMR indicates the formation of minor amounts of dimer **3**. The relative ratios **2/3** are 4.8:1 (MeOH), 12.5:1 (MeCN), 20:1 (i-PrOH), and > 20:1 (benzene).

Irradiation of 2 and 2,3-Dimethylbut-2-ene. Ar-degassed solns. of 10 mg (0.062 mmol) of **2** and 105 mg (1.24 mmol) of alkene in 2 ml of MeCN or benzene are irradiated for 24 h. After evaporation of the solvent, **2** is recovered quantitatively.

Irradiation of 2 and Tetrachloroethene. An Ar-degassed soln. of 48.6 mg (0.3 mmol) of **2** and 1.0 g (6 mmol) of tetrachloroethene in 5 ml MeCN is irradiated for 30 h. After evaporation of the solvent chromatography (SiO₂/CHCl₃) affords 44 mg (45%) *2ax,8bx-1,1,2,2-tetrachloro-2,2a-dihydro-1H-cyclobuta[c][2]benzothiopyran-4-one (4)*. M.p. 156–158°. ¹H-NMR (CDCl₃): 8.08 (*d*, $J = 8.0$); 7.59 (*t*, $J = 7.5$); 7.47 (*t*, $J = 7.5$); 7.31 (*d*, $J = 8.0$); 4.90, 4.72 (*AB*, $J = 10.2$). ¹³C-NMR (CDCl₃): 185.3 (*s*); 132.9 (*d*); 131.9 (*s*); 129.7 (*d*); 128.8 (*s*); 128.5 (*d*); 126.1 (*d*); 93.6 (*s*); 52.6 (*d*); 49.0 (*d*).

Quenching Experiment. To four Ar-degassed solns., each containing 2.3 mg (0.014 mmol) of **2** and 46 mg (0.28 mmol) of tetrachloroethene in 1 ml of MeCN, is added, respectively, 0 mg, 1.8 mg (0.014 mmol), 3.6 mg (0.028 mmol), and 7.2 mg (0.056 mmol) of naphthalene. The four solns. are then irradiated in a merry-go-round setup for 2 h. The slope of the straight-line resulting in the Φ_O/Φ vs. [naphthalene] diagram corresponds to 90 l/mol.

Irradiation of 1 and Tetrachloroethene. An Ar-degassed soln. of 48.6 mg (0.3 mmol) of **1** and 1.0 g (6 mmol) of alkene in 5 ml of MeCN is irradiated for 8 h. After evaporation of the solvent, chromatography (SiO₂/CH₂Cl₂) affords 27 mg (41%) of *2ax,8bx-1,1,2,2-tetrachloro-2,2a-dihydro-3H-cyclobuta[c][1]benzothiopyran-3-one (5)* as light yellow oil. ¹H-NMR (CDCl₃): 7.43–7.28 (*m*, 3 H); 7.14 (*d*, $J = 7.6$); 4.88, 4.05 (*AB*, $J = 10.2$).

Comparative Irradiations of 1 and 2 in the Presence of Alkenes. Two Ar-degassed solns., containing 46 mg (0.28 mmol) tetrachloroethene and 2.3 mg (0.014 mmol) of either **1** or **2** in 1 ml of MeCN, are irradiated in a merry-go-round setup for 4 h, and the formation of **5** (from **1**) and **4** (from **2**) is monitored by GC. The former reaction proceeds five times faster. Similarly, two Ar-degassed solns., containing 2.3 mg (0.014 mmol) of **1** and either 46 mg (0.28 mmol) of tetrachloroethene or 24 mg (0.28 mmol) of 2,3-dimethylbut-2-ene in 1 ml of MeCN, are irradiated for 45 min, the formation of the tetramethylethene cycloadducts proceeding 40 times faster than that of **5**.

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