87. Solid-State Photocyclodimerization of 1-Thiocoumarin (= 2*H*-1-Benzothiopyran-2-one)

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Dedicated to Prof. *Hans-Dieter Scharf*, TU Aachen, on the occasion of his 65th birthday

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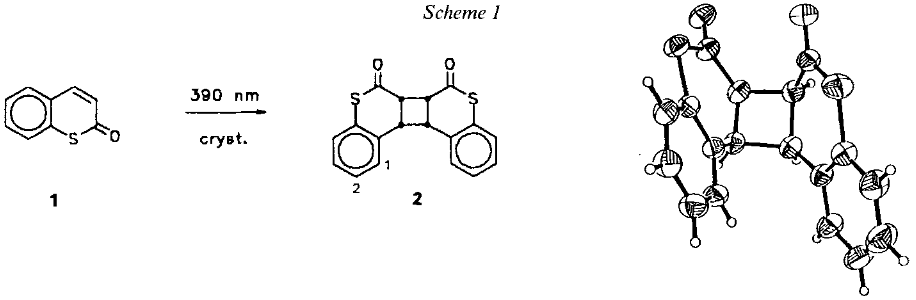
Irradiation ($\lambda > 390$ nm) of 2*H*-1-benzothiopyran-2-one (**1**) in the solid state affords selectively 6aα,6bα,12bα,12cα-tetrahydrocyclobuta[1,2-*c*:4,3-*c*′]bis[1]benzothiopyran-6,7-dione (**2**), the head-to-head (*HH*) *cis-cisoid-cis*-dimer, while irradiation of **1** in the solid state using *shorter* wavelengths ($\lambda > 340$ nm) affords a mixture of all four *cis*-fused tricyclic dimers **2**–**5**. These results represent a novel wavelength effect in solid-state photochemistry.

Introduction. – Solid-state photocyclodimerizations of cinnamic acids [1] and coumarins [2] were studied extensively. So-called 'topochemical rules' emerged from these and related studies, and the importance of defect sites in non-topochemical dimerizations was recognized, leading *inter alia* to crystal engineering [3] [4]. Interestingly, the reactive excited state was almost never reported for dimerization reactions in crystals [4] and, therefore, it is not surprising that wavelength effects in solid-state photochemistry have not been investigated up to now. In this paper, we report on the wavelength-dependent product distribution in the solid-state photocyclodimerization of 1-thiocoumarin (= 2*H*-1-benzothiopyran-2-one; **1**).

Results. – Irradiation ($\lambda > 390$ nm) of 1-thiocoumarin (**1**) as a solid film – obtained by evaporation of the solvent from an Et_2O solution – leads to the exclusive formation of the *HH-cis-cisoid-cis*-photocyclodimer[2] **2** which is isolated by chromatography in 30%

Scheme 1



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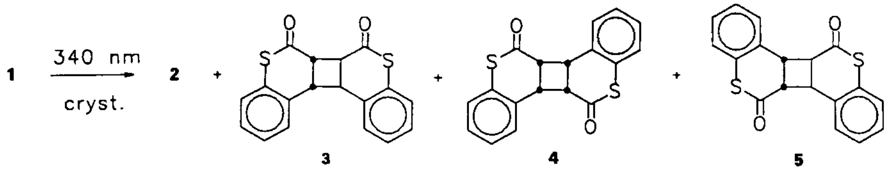
[2] Formerly, *syn* and *anti* were used for *cisoid* and *transoid*, respectively; *H* = head, *T* = tail.

yield and whose structure is confirmed by X-ray analysis (*Scheme 1*). This formation of **2** is complementary to that of the *HH-cis-transoid-cis*-dimer2) **3**, formed selectively on irradiation of **1** in solution, in MeCN, C_6H_6, or CH_2Cl_2 as solvent [5] [6].

Using light of shorter wavelength (λ > 340 nm) in the solid-state irradiation of **1** leads to the – unselective – formation of **2**, **3**, and the (new) *HT*-dimers2) **4** and **5** in a 10:11:1:3 ratio (*Scheme 2*). Monitoring the reaction by ^{1}H-NMR indicates that this product ratio remains constant up to 75% conversion of **1**. From this point onward, the relative amount of *both cis-cisoid-cis*-dimers **2** and **4** decreases. This effect can be accelerated by using light of 300 nm which reconverts both **2** and **4** to **1**. The structure assignment for **4** and **5** stems from ^{1}H-NMR analysis of the dimer mixture in $CDCl_3$, where all the *AA'XX'* signals of the cyclobutane protons resonate at different chemical shifts (*Fig.*).

Scheme 2



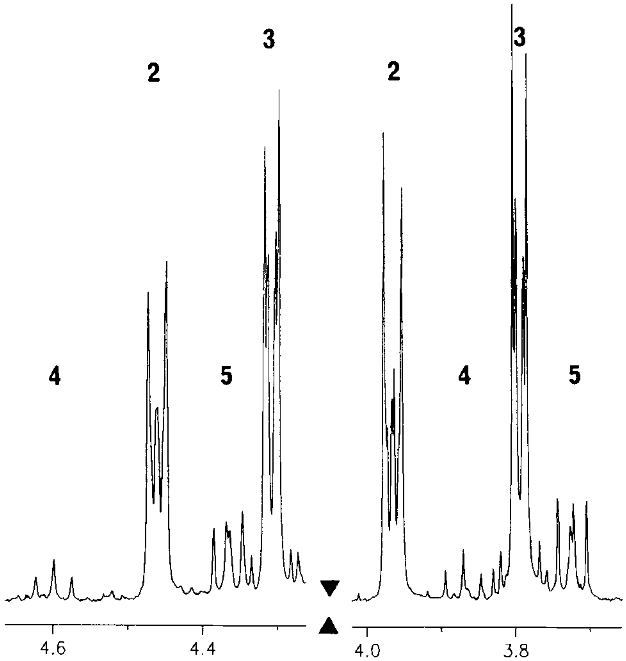


Figure. *^{1}H-NMR Spectrum* ($CDCl_3$, 400 MHz; cyclobutane-ring H-atoms) *of the mixture of photocyclodimers* **2–5** *in* $CDCl_3$

Discussion. – The selective formation of *HH-cis-cisoid-cis*-photocyclodimers in solid-state irradiations of cinnamic acids or substituted coumarins occurs quite frequently. These – topochemical – reactions occur with minimum atomic movements and take place, if the reactive double bonds are within the correct distance and aligned in a parallel fashion [4]. The conversion of **1** to **2** on irradiation with light of > 390 nm proceeds accordingly, the prealignment favoring this one dimer to the exclusion of others, albeit coumarin itself is photostable in the solid state and only affords the corresponding *HH-cis-cisoid-cis*-dimer when admixing crystal-lattice-controlling substances [7].

In contrast, the wavelength dependence observed in the irradiations with light > 340 nm is most unusual and apparently inprecedented. The fact that the product ratio **2**–**5** remains constant up to a reasonably high degree of conversion excludes reactions at melt sites, *i.e.*, that photodimerization is occurring in a liquid regime, since melting is more likely with increased conversion. It is, therefore, conceivable that excitation at 340 nm populates *two* excited states. If one of them has a much longer lifetime, this would allow exciton migration to defect sites, leading to the – observed – non-topochemical behavior.

Finally, the – relative – thermal and photochemical instability of *cis-cisoid-cis*-photodimers, *e.g.* **2** and **4**, as compared to the *cis-transoid-cis*-diastereoisomers, has precedents in the literature [8] [9].

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Experimental Part

General. The 2*H*-1-benzothiopyran-2-one (**1**) is synthesized according to [10] and purified by chromatography (SiO_2/CH_2Cl_2). Photolyses are performed with a 250-W high-pressure mercury lamp in combination with a liquid filter solution of either 75 g $NaNO_2$ 1 H_2O ($\lambda > 390$ nm; filter *A*) or 7 g $Pb(NO_3)_2$ and 750 g NaBr in 1 H_2O ($\lambda > 340$ nm; filter *B*) at r.t. ^{1}H-NMR Spectra: at 400 MHz; chemical shifts of cyclobutane H-atoms in ppm rel. to Me_4Si (= 0 ppm), coupling constants *J* in Hz. X-Ray analysis: *Enraf-Nonius-CAD-4* four-circle diffractometer with CuK_α radiation ($\lambda = 1.54178$ Å) at 293 K.

Solid-State Irradiation of **1** *with* $\lambda > 390$ *nm*. A soln. of 81 mg ($5 \cdot 10^{-4}$ mol) of **1** in 10 ml of Et_2O (25-ml tapered flask) is slowly evaporated to produce a homogeneous solid film. The flask is then purged with Ar, fixed next to the immersion wall (filter *A*) of the lamp and turned around from time to time. After 140 h, ^{1}H-NMR of the solid residue indicates an equimolar mixture of **1** and **2**. Chromatography (SiO_2/CH_2Cl_2) affords first 49 mg of **1** and then 25 mg (30%) of *6aα,6bα,12bα,12cα-tetrahydrocyclobuta[1,2-* c*:4,3-c′]bis[1]benzothiopyran-6,7-dione* (**2**). M.p. 215–217°. ^{1}H-NMR ($CDCl_3$): 4.46, 3.96 ($AA'XX'$, $J_{AX} = 10.5$, $J_{AA'} = 11.7$, $J_{XX'} = 6.1$, $J_{AX'} = -1.0$).

X-Ray Analysis of **2**. Pale yellow transparent blocks, 0.40 × 0.30 × 0.30 mm, were obtained by recrystallization from pentane. Crystal data: $C_{13}H_{12}O_2S_2$, $M_r = 324.4$, monoclinic, $P2_1/c$; $a = 11.844$ (1), $b = 13.479$ (1), and $c = 9.459$ (1), Å, $\beta = 94.32°$ (1), $v = 1505.8$ (2) Å^3, $Z = 4$, $D_x = 1.431$ Mg m^{-3}. The cell parameters were determined by least-square refinement against the setting angle of 25 reflections, $\Theta = 39.6$–$47.8°$, $\Theta_{max} = 76.5°$. Of the 2999 independent reflections, 2420 were considered to be observed [$I > 2\sigma(I)$], $R[F > 4\sigma(F)] = 0.0920$ (refinement on F^2). Crystallographic data were deposited with the *Cambridge Crystallographic Data Center*, University Chemical Laboratory, 12 Union Road, Cambridge CB2 1EZ, England.

Solid-State Irradiation of **1** *with* $\lambda > 340$ *nm*. Running the experiment as above (filter *B*) affords **2**/**3** [5] **4**/**5** in a 10:11:1:3 ratio (^{1}H-NMR).

6aα,6bα,12aα,12bα-Tetrahydrocyclobuta[1,2-c:3,4-c′]bis[1]benzothiopyran-6,12-dion (**4**): ^{1}H-NMR ($CDCl_3$; from **2**/**3**/**4**/**5**): 4.60, 3.87 ($AA'XX'$, $J_{AX} = J_{AX'} = 9.7$, $J_{AA'} = J_{XX'} = 0$).

6aα,6bβ,12aβ,12bα-Tetrahydrocyclobuta[1,2-c:3,4-c′]bis[1]benzothiopyran-6,12-dione (**5**): ^{1}H-NMR ($CDCl_3$; from **2**/**3**/**4**/**5**): 4.37, 3.72 ($AA'XX'$, $J_{AA'} = 3.5$, $J_{XX'} = 2.5$, $J_{AX'} = 9.6$, $J_{AX'} = 5.9$).

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