Site Selectivity in [2 + 2] Photocycloadditions of Tricyclic 'Diethenylbenzenes' to 2,3-Dimethylbut-2-ene

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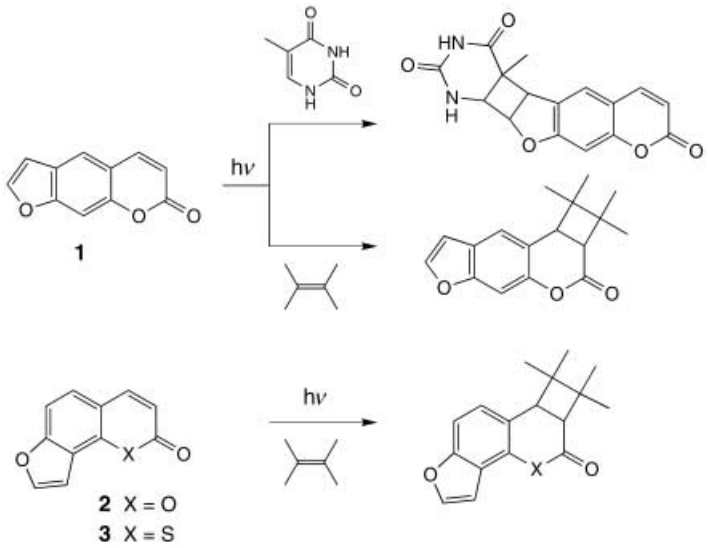
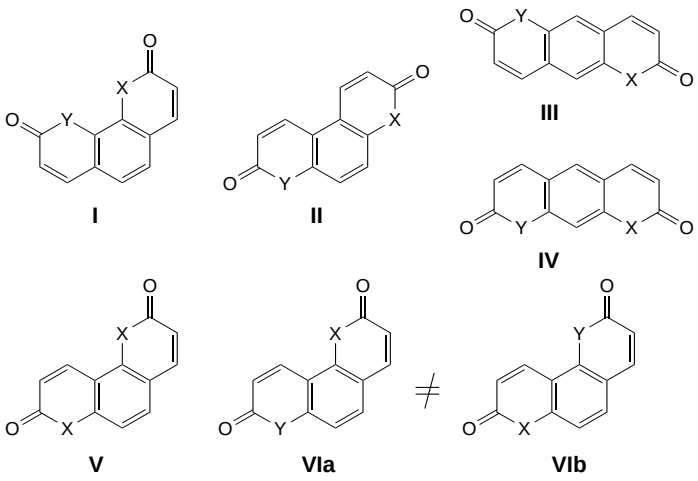
Upon irradiation at wavelengths above 390 nm in the presence of 2,3-dimethylbut-2-ene, both the newly synthesized pyranoquinolinedione **8** and thiinobenzopyrandione **9** selectively afford one of two possible photocycloadducts, **23** and **24**, respectively.

Introduction. – Crosslinking of thymine units within helical DNA strands can be achieved, for instance, by light-induced reactions of psoralens (2*H*-furo[3,2-*g*]benzopyran-2-ones), such as **1**, *via* two consecutive [2 + 2] photocycloadditions, the first one occuring at the furan double bond [1]. In contrast, photocycloadditions in solution of both linear (**1**) [2] and angular tricycles (**2** and **3**) [3] to alkenes selectively occur at the double bond of the six-membered heterocycle. This difference in selectivity has been attributed to the observation that the photocycloaddition to a nucleic acid is preceded by intercalation of a psoralen, the smaller furan moiety fitting into the helix [1] (*Scheme 1*).

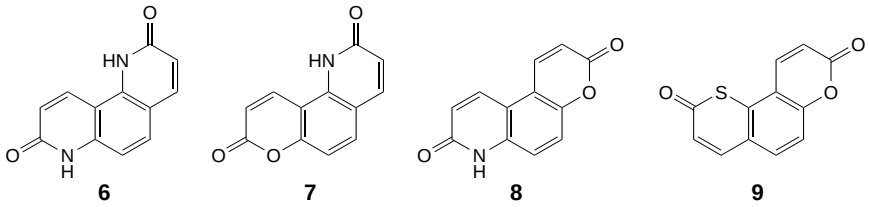
Scheme 1



Some years ago, we began to investigate the site-selectivity in [2+2] photocycloadditions using divinylbenzenes containing two *a priori* different olefinic moieties in tricyclic model compounds, wherein a (central) benzene ring is fused to two six-membered heterocyclic ring systems, containing either a lactone, a thiolactone or a lactam functionality. As shown in *Fig. 1*, compounds of type **I**–**IV** possess two different heteroatoms in symmetric positions. However, in compounds of type **V**, exchanging one heteroatom (X → Y) gives rise to two constitutional isomers (**VIa** *vs.* **VIb**) for symmetry reasons.

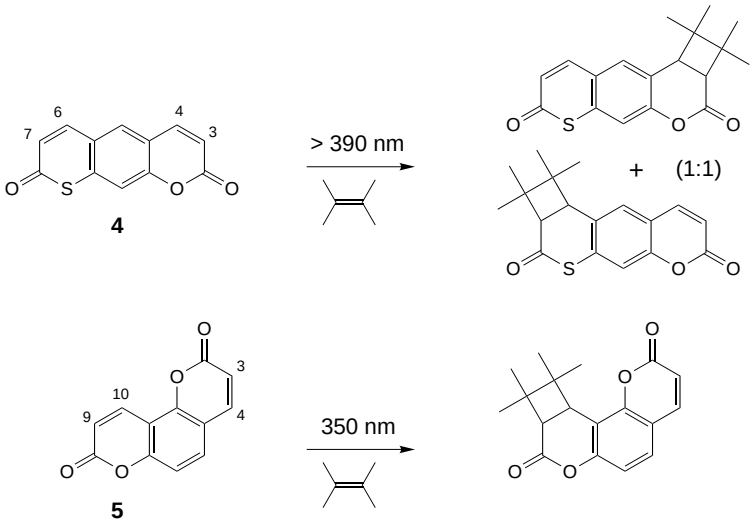


In this context, we reported that compound **4** undergoes photocycloaddition to 2,3-dimethylbut-2-ene at both double bonds [4], while compound **5** selectively reacts at the C(9)=C(10) bond [5] (*Scheme 2*). We now report the synthesis of the four novel tricycles **6**–**9** (*Fig. 2*) and (partially) their photochemical behavior.



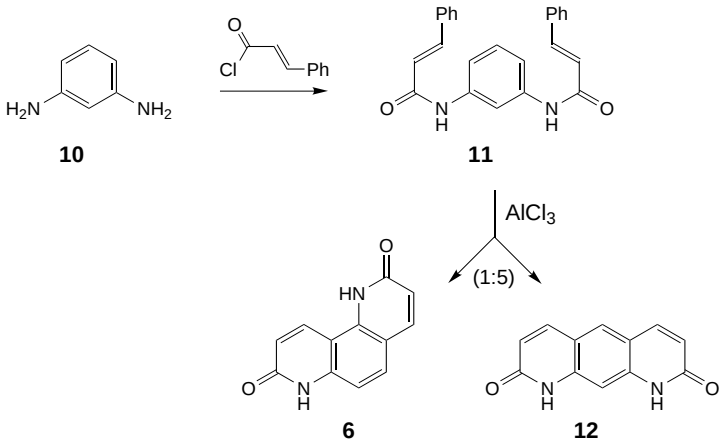
Results. – Phenanthroline-1,7-dione (**6**) was selected as the first target molecule. The synthetic approach started with benzene-1,3-diamine (*Scheme 3*), which was acylated with 3-phenylacrylic acid to **11**. The latter was expected to preferentially yield angular **6**, as observed in the formation of the analog **5** from 7-hydroxycoumarin and malic acid [6]. Unfortunately, the double cyclization of **11** mainly led to linear **12** with only minor amounts of **6** (*ca.* 15%) being formed. The purification of the corresponding mixture afforded pure **12** but led to the loss of the desired product.

Scheme 2



4 **5**

Scheme 3

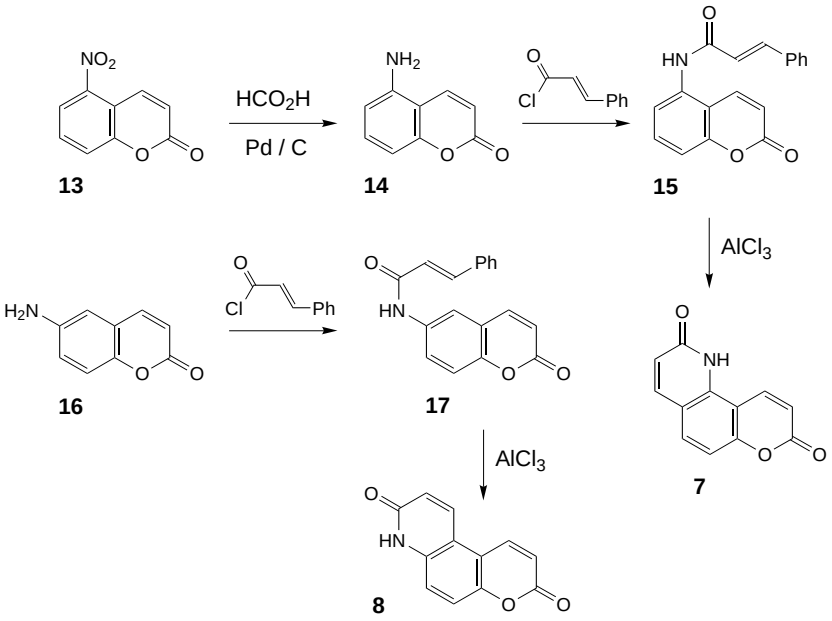


10 **11** **6** **12**

We next worked on the synthesis of the pyranoquinolinedione **7** starting with 5-nitro[1]benzopyran-2(2*H*)-one (5-nitrocoumarin) (**13**) (*Scheme 4*). Reduction with formic acid in the presence of Pd on charcoal gave **14**, which was converted to **7** *via* the cinnamoylamide **15**. Surprisingly, a similar reaction sequence, starting with the isomeric compound **16**, afforded the pyranoquinolinedione **8** in high yield by regioselective cyclization of **17** at C(5) of the benzopyran ring.

The thiinobenzopyran **9**, a monosulfur analog of **5**, was prepared according to [7]. Starting with the benzopyran **18**, extensive bromination afforded the dibromomethyl derivative **19**, which was hydrolyzed to the corresponding aldehyde **20**. Substitution of the NO_2 group by a (*tert*-butyl)sulfanyl group yielded **21**, which was subjected to a

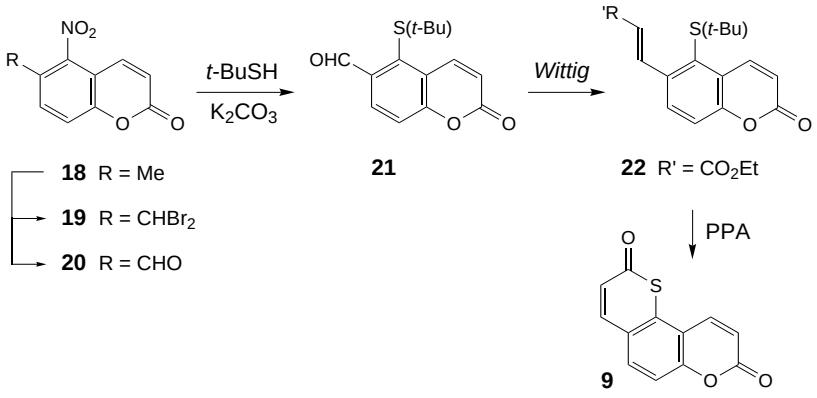
Scheme 4



Wittig reaction, affording the acrylate **22**. Finally, thiolactonization in the presence of polyphosphoric acid (PPA) led to **9** (*Scheme 5*).

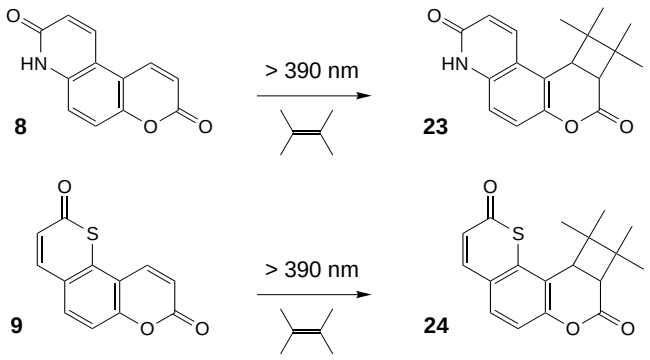
Irradiations of the tricycles **7**–**9** in the presence of a twentyfold molar excess of 2,3-dimethylbut-2-ene were performed at long wavelengths ($\lambda > 390$ nm) to avoid consecutive photocycloadditions of the primary products. Both the N-containing heterocycles **7** and **8** were reasonably soluble only in pyridine, whereas **9** was readily dissolved in MeCN. Irradiation of **7** for 18 h did not lead to any product formation. Therefore, the experiment was repeated with light of shorter wavelength ($\lambda > 340$ nm).

Scheme 5



However, after 2 h, the starting material was completely converted into a mixture of two bis-cycloadducts and one product arising from decarbonylation, as monitored by ^{1}H-NMR. In contrast, both **8** and **9** selectively and exclusively afforded at $\lambda > 390$ nm the monocycloadducts **23** and **24**, respectively (*Scheme 6*). The structural assignment of **23** was achieved by comparing the chemical shifts of the carbonyl C-atoms in the ^{13}C-NMR spectrum (167 and 163 ppm), which clearly correlate with those of 3,4-dihydrocoumarin [8] and of quinolone [9] (168 ppm and 164 ppm) but not with coumarin [8] and 3,4-dihydroquinolone [10] (160 ppm and 172 ppm), respectively. For **24** (δ (S–*C*=O) = 183 ppm), the same criteria can be used to differentiate between a thiocoumarin and a 3,4-dihydrothiocoumarin (185 ppm and 199 ppm [11]). In addition, the vicinal ^{1}H-NMR coupling constant in the unsaturated six-membered ring (J = 10.6 Hz) clearly indicates a remaining (unsaturated) thiopyranone and not a pyranone moiety (J = 10.6 *vs.* 9.8 Hz).

Scheme 6



Discussion. – An unexpected inconvenience in working with the N-containing heterocycles **7** and **8** turned out to be their very low solubility in common organic solvents. Recrystallization was only possible from glacial acetic acid, and NMR-spectra had to be measured in deuterated pyridine. This problem also concerned the photolyses, since product separation and purification was difficult. A second, more general problem arises from conventional cyclization reactions for the formation of thiocoumarins or quinolones not often being applicable to the synthesis of compounds containing *two* heterocyclic rings fused to one central benzene unit.

The selective formation of **24** in the photocycloaddition of **9** to 2,3-dimethylbut-2-ene parallels the corresponding reaction with the bis-lactone **5** (*Scheme 2*), since only the C=C bond closer to the heteroatom of the second heterocycle turns out to be reactive. This finding underscores that only *ortho*- and *meta*-transmission is characteristic of the first excited state of both substituted benzenes [12] and ethenylbenzenes [13], *i.e.*, electron donors increase the π-electron densities at both the *ortho*- and *meta*- but not at the *para*-position.

In contrast, the selective formation of **23** in the photocycloaddition of **8** to 2,3-dimethylbut-2-ene does not reflect the behavior of the (symmetric) tricycle **4**

(*Scheme 2*), in which both double bonds of the heterocycles proved to be reactive. Since these reactions were run in different solvents (MeCN *vs.* pyridine), the above results cannot be generalized at the moment without additional experiments.

Experimental Part

1. *General. Benzene-1,3-diamine* (**10**) was commercially available. The benzopyranones 5-nitro- (**13**) [14], 6-amino- (**16**) [15], and 6-methyl-5-nitro[1]benzopyran-2(2*H*)-one (**18**) [16] were prepared according to literature procedures.

UV Spectra: MeCN, λ in nm (log ε). ^{1}H- and ^{13}C-NMR Spectra: 500 and 125.8 MHz, resp.; chemical shifts δ in ppm rel. to Me_4Si (=0 ppm). EI-MS: 70 eV; in *m*/*z* (rel. intensity in % of base peak). Photolyses were performed in an immersion well, a 250 W high-pressure Hg-lamp being used together with a liquid filter (75 g $NaNO_2$/1000 ml H_2O), transparent to light of $\lambda > 390$ nm.

2. *Attempted Synthesis of 1,2,7,8-Tetrahydro-1,7-phenanthroline-2,8-dione* (**6**). 2.1. N,N′*-[Benzene-1,3-diyl]bis[3-phenylprop-2-enamide]* (**11**). Prepared in analogy to the acylation procedure described in [17]: To an ice-cooled soln. of benzene-1,3-diamine (**10**, 1.08 g, 10 mmol) and K_2CO_3 (4.15 g, 30 mmol) in a mixture of H_2O (40 ml) and acetone (20 ml) was added in small portions 3-phenylprop-2-enoyl chloride (cinnamoyl chloride) (4.1 g, 25 mmol). The mixture was then stirred for 1 h at 0° and poured into iced H_2O (100 ml). The precipitate was filtered off and recrystallized from EtOH, affording 2.26 g (62%) of **11**. M.p. 207°.^{1}H-NMR ($(CD_3)_2SO$): 10.26 (*s*, 2 H); 8.13 (*s*, 1 H); 7.60 (*d*, *J* = 15.8, 2 H); 7.59–7.38 (*m*, 12 H); 7.29 (*t*, *J* = 8.1, 1 H); 6.89 (*d*, *J* = 15.8, 2 H). ^{13}C-NMR ($(CD_3)_2SO$): 163.9 (*s*); 140.4 (*d*); 140.0 (*s*); 135.1 (*s*); 130.1 (*d*); 129.4 (*d*); 129.3 (*d*); 128.1 (*d*); 122.8 (*d*); 114.8 (*d*); 110.5 (*d*). EI-MS: 368 (34, $M^{+\bullet}$), 131 (100).

2.2. *Cyclization of* **11** *Affording 1,2,8,9-Tetrahydropyrido[3,2-*g*]quinoline-2,8-dione* (**12**). Prepared in analogy to the cyclization procedure described in [18]: To an ice-cooled suspension of **11** (368 mg, 1 mmol) in 1,2-dichlorobenzene (20 ml) was added in small portions $AlCl_3$ (3.0 g, 22.5 mmol). The mixture was heated at 150° for 3 h and was poured after cooling into ice-water (100 ml). The precipitate was filtered and washed with hot acetone (3 ×) to afford 106 mg (50%) of a 1:5-mixture of **6**/**12** as verified by ^{1}H-NMR. On recrystallization from glacial acetic acid, pure **12** (71 mg, 34%) was obtained. M.p. >370° (>400° [19]). ^{1}H-NMR ((D_5)-Pyridine): 7.78 (*d*, *J* = 9.5, 2 H); 7.73 (*s*, 1 H); 7.34 (*s*, 1 H); 6.75 (*d*, *J* = 9.5, 2 H). EI-MS: 212 (100, $M^{+\bullet}$).

3. *Synthesis of 1,2-dihydropyrano-[2,3-*h*]quinoline-2,8(8*H*)-dione* (**7**). 3.1. *5-Amino[1]benzopyran-2(2*H*)-one* (**14**). In analogy to the reduction procedure described in [16]: A mixture of **13** (1.91 g, 10 mmol) and Pd on charcoal (0.6 g) in Et_3N (100 ml) and HCO_2H (12 ml) was heated at 100° for 2 h. After cooling to r.t. the mixture was poured into iced H_2O (250 ml) and extracted with $CHCl_3$ (3×). The combined org. layers were dried ($MgSO_4$), and the solvent was evaporated. Recrystallization of the solid residue from EtOH afforded 970 mg (60.5%) of **14**. M.p. 148°.^{1}H-NMR ($CDCl_3$): 7.76 (*d*, *J* = 9.7); 7.28 (*t*, *J* = 8.1); 6.73 (*d*, *J* = 8.1); 6.55 (*d*, *J* = 8.1); 6.32 (*d*, *J* = 9.7); 4.14 (br. *s*, 2 NH). ^{13}C-NMR ($CDCl_3$): 161.0 (*s*); 155.4 (*s*); 143.9 (*s*); 137.6 (*d*); 132.7 (*d*); 113.8 (*d*); 110.6 (*d*); 107.1 (*d*); 106.7 (*s*). EI-MS: 161 (100, $M^{+\bullet}$).

3.2. N*-(2-Oxo-2*H*-[1]benzopyran-5-yl)-3-phenylprop-2-enamide* (**15**). As in *Sect. 2.1*, **14** (805 mg, 5 mmol) afforded 1.1 g (75%) of **15**. M.p. 233°. ^{1}H-NMR ($(CD_3)_2SO$): 10.28 (*s*, NH); 8.19 (*d*, *J* = 9.9, 1 H); 7.65 (*d*, *J* = 15.8, 1 H); 7.64–7.40 (*m*, 7 H); 7.23 (*d*, *J* = 8.1, 1 H); 7.01 (*d*, *J* = 15.8, 1 H); 6.54 (*d*, *J* = 9.9, 1 H). ^{13}C-NMR ($(CD_3)_2SO$): 164.2 (*s*); 159.5 (*s*); 154.1 (*s*); 140.9 (*d*); 140.1 (*d*); 135.4 (*s*); 134.5 (*s*); 131.8 (*d*); 129.9 (*d*); 129.0 (*d*); 127.7 (*d*); 121.4 (*d*); 119.5 (*d*); 115.0 (*d*); 112.8 (*d*); 112.5 (*s*).

3.3. *Cyclization.* As in *Sect. 2.2*, **15** (582 mg, 2 mmol) afforded 170 mg (40%) of **7**. M.p. >370° (AcOH). UV: 358 (sh, 3.50), 302 (3.90), 272 (3.91), 231 (4.12). ^{1}H-NMR ((D_5)-Pyridine): 9.40 (*d*, *J* = 9.9); 7.84 (*d*, *J* = 9.7); 7.71 (*d*, *J* = 8.7); 7.11 (*d*, *J* = 8.7); 6.82 (*d*, *J* = 9.7); 6.72 (*d*, *J* = 9.9). ^{13}C-NMR ((D_5)-Pyridine): 163.9 (*s*); 160.8 (*s*); 155.9 (*s*); 141.0 (*d*); 139.5 (*d*); 138.1 (*s*); 132.0 (*d*); 121.7 (*d*); 116.9 (*s*); 115.9 (*s*); 115.1 (*d*); 111.7 (*d*). EI-MS: 213 (100, $M^{+\bullet}$).

4. *Synthesis of 3,4,7,8-Tetrahydropyrano[3,2-*f*]quinoline-3,8-dione* (**8**). 4.1. N*-(2-Oxo-2*H*-[1]benzopyran-6-yl)-3-phenylprop-2-enamide* (**17**). As in *Sect. 2.1*, **16** (805 mg, 5 mmol) afforded 1.2 g (83%) of **17**. M.p. 225–228° (EtOH). ^{1}H-NMR ($(CD_3)_2SO$): 10.47 (*s*, NH); 8.16 (*d*, *J* = 2.6, 1 H); 8.11 (*d*, *J* = 9.7, 1 H); 7.80 (*dd*, *J* = 2.6, 9.2, 1 H); 7.63 (*d*, *J* = 15.8, 1 H); 7.62–7.37 (*m*, 6 H); 6.85 (*d*, *J* = 15.8, 1 H); 6.50 (*d*, *J* = 9.2, 1 H). ^{13}C-NMR ($(CD_3)_2SO$): 163.6 (*s*); 159.9 (*s*);149.4 (*s*); 144.3 (*d*); 140.4 (*d*); 135.6 (*s*); 134.5 (*s*); 129.8 (*d*); 128.9 (*d*); 127.7 (*d*); 123.3 (*d*); 121.8 (*d*); 118.7 (*s*); 117.7 (*d*); 116.6 (*d*); 116.5 (*d*). EI-MS: 291 (11, $M^{+\bullet}$). 131 (100).

4.2. *Cyclization.* As in *Sect. 2.2*, **17** (582 mg, 2 mmol) afforded 128 mg (34%) of **8**. M.p. >370° (AcOH). UV: 384 (3.11), 366 (3.24), 316 (3.75), 304 (3.82), 239 (4.37). ^{1}H-NMR ((D_5)-Pyridine): 8.44 (*d*, *J* = 9.7); 8.33

(d, J = 9.7); 7.70 (d, J = 8.9); 7.46 (d, J = 8.9); 7.03 (d, J = 9.7); 6.70 (d, J = 9.7). ^{13}C-NMR ((D$_5$)-Pyridine): 162.6 (s); 160.3 (s); 150.3 (s); 139.1 (d); 137.5 (s); 134.6 (d); 124.8 (d); 120.0 (d); 119.9 (d); 117.8 (d); 115.2 (s); 115.1 (s). EI-MS: 213 (100, $M^{+\cdot}$).

5. *Synthesis of 1,2,7,8-Tetrahydrothiino[2,3-f][1]benzopyran-2,8-dione* (**9**). 5.1. *6-(Dibromomethyl)-5-nitro[1]benzopyran-2(*2H*)-one* (**19**). Prepared in analogy to [20]: A soln. of **18** (8.2 g, 40 mmol), 1-bromopyrrolidine-2,5-dione (NBS) (35.2 g, 0.2 mol), and dibenzoylperoxide (5 g) in CCl_4 (200 ml) was heated under N_2 for 8 h. Heating was continued for another 8 h after additional NBS and peroxide had been added. The hot mixture was filtered, and the filtrate was evaporated. The residue was purified by column chromatography (CC) (SiO_2; hexane/AcOEt 3 :1) to afford 3.65 g (25%) of **19** as a yellow oil. R_f 0.48. ^{1}H-NMR ($CDCl_3$): 8.29 (d, J = 9.2); 7.66 (d, J = 9.9); 7.62 (d, J = 9.2); 6.76 (s); 6.63 (d, J = 9.9).

5.2. *5-Nitro-2-oxo-2*H*[1]benzopyran-6-carbaldehyde* (**20**). Compound **19** (3.63 g, 10 mmol) was suspended in a soln. of K_2CO_3 (1 g) in H_2O, (400 ml) and the mixture was refluxed for 2 h. After cooling to 5°, the precipitate was filtered and dried, affording 1.21 g (55%) of **20**. M.p. 178–180°. ^{1}H-NMR ((D$_6$)-Acetone): 10.08 (s); 8.34 (d, J = 8.6); 7.89 (d, J = 10.4); 7.81 (d, J = 8.6); 6.77 (d, J = 10.4). EI-MS: 219 (22, $M^{+\cdot}$), 189 (100).

5.3. *5-[(*tert*-Butyl)sulfanyl]-2-oxo-2*H*-[1]benzopyran-6-carbaldehyde* (**21**). Prepared in analogy to the nucleophilic displacement procedure described in [7]: To a soln. of **20** (1.1 g, 5 mmol) in DMF (20 ml) under N_2, K_2CO_3 (2.2 g, 15 mmol) and 2-methylpropane-2-thiol (1.4 g, 15 mmol) were added. The mixture was heated at 90° for 24 h. The above procedure (addition of reagents and heating) was repeated. The mixture was cooled to r.t., poured into H_2O (150 ml), acidified with dil. aq. HCl to pH 2, and extracted with $CHCl_3$ (4 ×). The combined org. layers were washed with H_2O, dried ($MgSO_4$), and the solvent was evaporated. The residue was purified by CC (SiO_2; hexane/AcOEt 3 :1) to afford 655 mg (50%) of **21**. R_f 0.48. M.p. 113°. ^{1}H-NMR ($CDCl_3$): 10.80 (s); 8.71 (d, J = 9.9); 8.20 (d, J = 8.9); 7.48 (d, J = 8.9); 6.55 (d, J = 9.9); 1.28 (s, t-Bu). ^{13}C-NMR ($CDCl_3$): 192.0 (d); 159.4 (s); 157.9 (s); 142.1 (d); 137.4 (s); 137.0 (s); 131.1 (d); 124.0 (s); 118.8 (d); 117.2 (d); 50.7 (s); 31.1 (q). EI-MS: 262 (4, $M^{+\cdot}$). 57 (100).

5.4. *Ethyl 3-{5-[(*tert*-Butyl)sulfanyl]-2-oxo-2*H*-[1]benzopyran-6-yl}prop-2-enoate* (**22**). Prepared in analogy to the *Wittig*-type procedure described in [21]: A soln. of **21** (524 mg, 2 mmol) and ethyl 2-(triphenylphosphoranylidene)acetate (1.4 g, 2 mmol) in benzene (25 ml) was refluxed under N_2 for 24 h. After evaporation of the solvent, the residue was purified by CC (SiO_2; hexane/AcOEt 3 :1) to afford 600 mg (90%) of **22**. R_f 0.42. M.p. 113–115°. ^{1}H-NMR ($CDCl_3$): 8.69 (d, J = 9.7, 1 H); 8.64 (d, J = 16.3, 1 H); 7.90 (d, J = 8.6, 1 H); 7.40 (d, J = 8.6, 1 H); 6.49 (d, J = 9.7, 1 H); 6.40 (d, J = 16.3, 1 H); 4.30 (q, J = 7.1, 2 H); 1.36 (t, J = 7.1, 3 H); 1.26 (s, 9 H). ^{13}C-NMR ($CDCl_3$): 166.6 (s); 159.9 (s); 155.4 (s); 143.6 (d); 143.5 (d); 137.7 (s); 134.1 (s); 129.5 (d); 124.3 (s); 120.0 (d); 118.5 (d); 116.9 (d); 60.7 (t); 51.2 (s); 31.3 (q); 14.3 (q). EI-MS: 332 (1, $M^{+\cdot}$), 57 (100).

5.5. *Cyclization*. Prepared in analogy to the saponification/cyclization procedure described in [7]: A soln. of **22** (532 mg, 1.6 mmol) in EtOH (5 ml) was mixed with a soln. of KOH in H_2O (0.5 g/5 ml), and the mixture was refluxed for 1 h. After cooling, the mixture was extracted with Et_2O, and the aq. phase was neutralized with dil. aq. HCl. The precipitate was filtered, dried, and heated in the presence of polyphosphoric acid (PPA, 8 g) to 80° for 6 h. The mixture was cooled to 40° and poured into 100 ml of H_2O. The suspension was extracted with $CHCl_3$ (5 ×), the combined org. layers were washed with both aq. $NaHCO_3$ soln. and H_2O, and were dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by CC (SiO_2; Et_2O) to afford 73 mg (20%) of **9**. R_f 0.54. M.p. 214°. UV: 356 (3.55); 295 (4.23); 249 (4.08). ^{1}H-NMR ($CDCl_3$): 8.01 (d, J = 9.7); 7.76 (d, J = 10.7); 7.74 (d, J = 8.7); 7.36 (d, J = 8.7); 6.60 (d, J = 9.7); 6.59 (d, J = 10.7). ^{13}C-NMR ((CD$_3$)$_2$SO): 182.1 (s); 158.7 (s); 154.9 (s); 145.2 (d); 138.0 (d); 135.8 (s); 135.3 (d); 122.3 (s); 122.2 (d); 117.1 (d); 115.7 (d); 114.3 (s). EI-MS: 230 (79, $M^{+\cdot}$), 174 (100).

6. *Photolyses in the Presence of 2,3-Dimethylbut-2-ene*. 6.1. *Irradiation of* **8**. An Ar-degassed soln. of **8** (42.6 mg, 0.2 mmol) and the alkene (336 mg, 4 mmol) in pyridine (50 ml) was irradiated for 8 h. After evaporation of the solvent, the solid residue was washed with hot acetone and recrystallized from AcOH affording 40 mg (67%) of *2,2a,3,7,8,10c-hexahydro-1,1,2,2-tetramethyl-1*H*-cyclobuta[1,2:4′,5′]pyrano[3,2-f]quinoline-3,8-dione* (**23**). M.p. >350° (dec.). ^{1}H-NMR ((D$_5$)-Pyridine): 7.75 (d, J = 9.8); 7.45 (d, J = 8.8); 7.26 (d, J = 8.8); 6.96 (d, J = 9.8); 3.87 (d, J = 9.8); 3.34 (d, J = 9.8); 1.28 (s, Me); 1.23 (s, Me); 1.10 (s, Me); 0.66 (s, Me). ^{13}C-NMR ((D$_5$)-Pyridine): 167.1 (s); 162.9 (s); 147.1 (s); 137.8 (d); 136.7 (s); 124.6 (d); 121.8 (d); 118.5 (s); 118.0 (s); 116.2 (d); 43.5 (d); 43.1 (s); 43.0 (s); 40.0 (d); 27.0 (q); 26.0 (q); 22.9 (q); 21.5 (q). EI-MS: 297 (15, $M^{+\cdot}$), 84 (100).

6.2. *Irradiation of* **9**. An Ar-degassed soln. of **9** (46 mg, 0.2 mmol) and the alkene (336 mg, 4 mmol) in MeCN (50 ml) was irradiated for 10 h. After evaporation of the solvent, the residue was purified by CC (SiO_2; Et_2O) to afford 38 mg (60%) of *1,2,2a,3,9,10c-hexahydro-1,1,2,2-tetramethylcyclobuta[c]thiino[2,3-f]benzopyr-*

an-3,9-dione (**24**). R_f 0.64. M.p. 113–115°. ^{1}H-NMR ($CDCl_3$): 7.62 (d, J = 10.6); 7.44 (d, J = 8.5); 7.01 (d, J = 8.5); 6.42 (d, J = 10.6); 3.64 (d, J = 9.9); 3.11 (d, J = 9.9); 1.32 (s, Me); 1.29 (s, Me); 1.00 (s, Me); 0.72 (s, Me). ^{13}C-NMR ($CDCl_3$): 183.1 (s); 164.9 (s); 152.1 (s); 143.2 (d); 137.5 (s); 131.1 (d); 121.8 (s); 121.2 (d); 116.4 (s); 115.1 (d); 45.1 (s); 44.1 (s); 41.9 (d); 38.4 (d); 25.9 (q); 24.8 (q); 19.8 (q); 19.7 (q). EI-MS: 314 (7, $M^{+\cdot}$), 84 (100).

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Received September 8, 2001