105. Aromatic Nucleophilic Substitution

Part 3[1])

Preparation of Novel 9-Oxo-9*H*-thioxanthene- and 9-Oxo-9*H*-xanthenedicarboximides and -dicarboxylates

by **Walter Fischer**

Central Research Laboratories, *Ciba-Geigy AG*, CH–4002 Basel

(11.VI.91)

By aromatic nucleophilic substitution followed by intramolecular acylation, 9-oxo-9*H*-thioxanthene- and 9-oxo-9*H*-xanthene-dicarboximides were prepared from nitro- or chlorophthalimides and the dianions of thiosalicylic and salicylic acids (*Scheme*). The 9-oxo-9*H*-thioxanthene-3,4-dicarboximides were converted to 9-oxo-9*H*-thioxanthene-3,4-dicarboxylic-acid derivatives such as anhydride, esters, and further imides. Some of these derivatives proved to be excellent photosensitizers with special properties such as liquid aggregation form, H_2O solubility, solubility in lipophilic organic solvents and polymers, or bathochromic shifts of the absorption wavelengths.

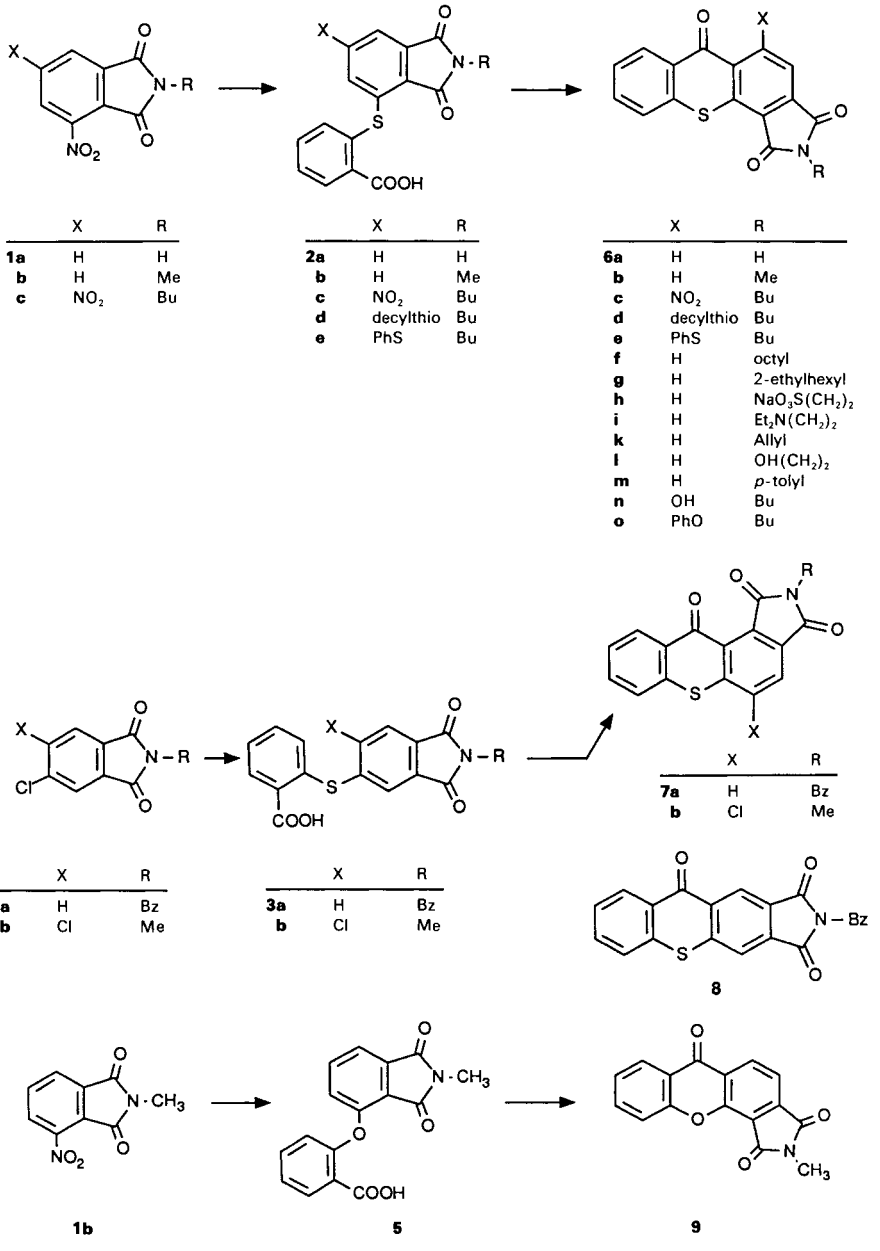
1. Introduction. – The 9*H*-thioxanthen-9-ones (= thioxanthones = 10*H*-dibenzo-[*b*,*e*]thiopyran-10-ones) are useful photoinitiators and photosensitizers in industrial applications [2]. In a preceding paper [1], we described the synthesis of novel thioxanthone and xanthone monoester derivatives whose properties could be adapted to the specific application by the introduction of suitable substituents. However, to reach further special properties, *e.g.* a liquid form, solubilities in H_2O or lipophilic solvents and polymers, or even more bathochromic shifts of the absorption wavelengths, the introduction of further functional groups was required. We now report the preparation of novel thioxanthone and xanthone derivatives with two vicinal carboxylic-acid functions in 1,2-, 2,3-, and above all, in 3,4-positions.

2. Syntheses. – *3-Arylthio-Substituted Phthalimides* **2a–e** *and* **3a,b** *and Diphenyl-Ether Derivative* **5** (*Scheme*). The NO_2 group in 3-nitrophthalimides **1a–c** was substituted by the disodium salt of 2-mercaptobenzoic acid (thiosalicylic acid) to prepare the intermediates **2a–c** in fair yields. In the case of dinitrophthalimide **1c**, the 3-NO_2 group was substituted chemo- and regioselectively. This behaviour is paralleled by the reaction with thiolates or phenolates reported earlier [3]. By subsequent reaction of the 5-NO_2-group with *in situ*-prepared decanethiolate or thiophenolate, the intermediates **2d,e** were accessible in good yields.

The Cl groups in phthalimides **4a,b** required more vigorous conditions to react with thiosalicylic acid dianion. The intermediates **3a,b** were used in the cyclisation step without further purification.

[1]) Part 2, see [1].

Scheme



	X	R
1a	H	H
b	H	Me
c	NO_2	Bu

	X	R
2a	H	H
b	H	Me
c	NO_2	Bu
d	decylthio	Bu
e	PhS	Bu

	X	R
6a	H	H
b	H	Me
c	NO_2	Bu
d	decylthio	Bu
e	PhS	Bu
f	H	octyl
g	H	2-ethylhexyl
h	H	$NaO_3S(CH_2)_2$
i	H	$Et_2N(CH_2)_2$
k	H	Allyl
l	H	$OH(CH_2)_2$
m	H	*p*-tolyl
n	OH	Bu
o	PhO	Bu

	X	R
7a	H	Bz
b	Cl	Me

	X	R
4a	H	Bz
b	Cl	Me

	X	R
3a	H	Bz
b	Cl	Me

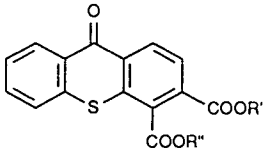
8

1b **5** **9**

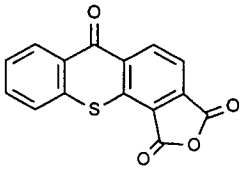
For the synthesis of **5** from **1b**, salicylic acid disodium salt was used as nucleophile, and rather vigorous conditions were required. Intermediate **5** was cyclized without further purification. With the NH-imide **1a** as starting electrophile, no substitution took place due to proton transfer from the rather acidic imide group to the phenolate.

*Cyclisation to the 9-Oxo-9*H*-thioxanthene- and 9-Oxo-9*H*-xanthene-imides* **6a–e**, **7a,b**, **8**, *and* **9** (*Scheme*). The intermediates **2**, **3**, and **5** were cyclised by heating in polyphosphoric acid (PPA) or by reacting the corresponding acyl chlorides with $AlCl_3$. With **3a**, the expected regioisomers **7a** and **8** were isolated and separated by column chromatography. The cyclisation of the nitro derivative **2c** to the nitrothioxanthone **6c** is noteworthy. Obviously, the donor capacity of the thioether function can partly compensate the π-acceptor effects of three strongly electron-withdrawing groups so that the intramolecular electrophilic substitution takes place.

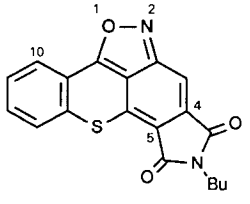
Variation of the Imide Function of **6a**. Hydrolysis of **6a** in alkaline aqueous solution and then in acidic aqueous suspension gave the dicarboxylic acid **10a** which was reacted with Ac_2O to the 9-oxo-9*H*-thioxanthene-3,4-anhydride **11**. Treatment of anhydride **11** with exactly 2 equiv. of aq. NaOH solution gave the H_2O soluble disodium salt **10b** upon evaporation. Ethanolysis of **11** gave the half esters **10c** and **10d** in a ratio of *ca.* 3:1 (^{1}H-NMR); **10c** could be isolated pure by fractional crystallisation. When **11** was heated in BuOH, a similar mixture of half esters was formed which was converted to the dibutyl ester **10e** by acid-catalysed esterification. This diester was still crystalline (m.p. 49–51°). To prepare a *liquid* thioxanthone, anhydride **11** was reacted with a 1:1 mixture of octanol/2-ethylhexanol under similar conditions. This gave a mixture of regio-, stereo-, and diastereoisomers **10f–i** which in fact is a clear viscous liquid stable so far over a long period of time with no sign of crystallisation.



	R'	R"
10a	H	H
b	Na	Na
c	Et	H
d	H	Et
e	Bu	Bu
f	octyl	octyl
g	octyl	2-ethylhexyl
h	2-ethylhexyl	octyl
i	2-ethylhexyl	2-ethylhexyl



11



12

Imide **6a** could be easily alkylated by octyl bromide to imide **6f**. Alternatively, anhydride **11** reacted smoothly with primary amines to give further alkylated and arylated imides **6g–m**.

Aromatic Nucleophilic Substitution of the Nitro Group in **6c**. The NO_2 group of **6c** is highly activated by the π-acceptor effects of the carbonyl and imide functions. Additionally, some steric distortion by the carbonyl group might increase the reactivity further as it is the case in 3,5-dinitrophthalimides and anhydrides [3] or in 2,4-dinitrotoluene [4]. Thus, the reaction with K_2CO_3 gave the hydroxy compound **6n**, whereas under similar conditions, but with phenol added, the phenoxy derivative **6o** was obtained in good yield.

The reaction of **6c** with NaN_3 proceeded smoothly at 25°. The intermediary aryl azide cyclised spontaneously with loss of N_2 to give the novel quinonoid heterocyclic system **12**. This reaction has some precedents in the field of anthraquinone azides [5].

With decanethiolate and thiophenolate anions, the thioether derivatives **6d,e** were also accessible by this alternate route.

3. Properties. – *Physical Properties.* A wide range of melting points and solubilities is covered by these products. The H_2O-soluble salts **10b** and **6h** do not melt or decompose up to 330°. Salt **10b** is soluble in neutral and alkaline aqueous solution, whereas **6h** is soluble over a wide pH range. Most other derivatives are soluble in organic solvents. The liquid diester mixture **10f–i** is especially well soluble in even lipophilic solvents and polymers and is thus very useful for technical applications.

The 1-unsubstituted oxothioxanthene-3,4-dicarboximides **6a,b** and **6f–m** have their longest-wavelength absorptions (λ_{max}) at *ca.* 420 nm with absorption coefficients (ε) around 5000 (see *Exper. Part*). As expected, little influence can be seen by alkyl groups at the N-atom. Compared to unsubstituted thioxanthone (382 nm), the introduction of the 3,4-dicarboximide function gives a bathochromic shift of 38 nm. The 1,2-dicarboximide **7a** (405 nm) and the 2,3-dicarboximide **8** (407 nm) exhibit smaller bathochromic shifts compared to the parent thioxanthone. The analogous oxoxanthene-3,4-dicarboximide **9** absorbs at much shorter wavelength (372 nm). Substituents in 1-position of the oxothioxanthene-3,4-dicarboximide have either little effect (**6o** (X = PhO): 417 nm) or induce bathochromic shifts, independent of their electronic nature (donor or acceptor; **6c** (X = NO_2): 430 nm; **6n** (X = OH): 440 nm; **6e** (X = PhS): 453 nm; **6d** (X = decylthio): 456 nm).

The half ester **10c** as well as the diesters **10e** and **10f–i** and the disodium dicarboxylate **10b** absorb almost identically between 394 and 397 nm. These smaller effects might be attributed to some steric interactions between the functional groups which at least partly affect their conjugation with the chromophor by turning them out of the chromophor plane.

The novel heterocyclic system **12** exhibits two absorptions in the VIS at 427 (ε 12900) and 451 nm (ε 11000).

Photochemical Properties. When tested in a photoresist material containing pendent dimethylmaleinimide units as photosensitive functional groups [6], some of the imides (**6a,b,f,k**) and the diesters (**10e** and **10f–i**) exhibited excellent properties as triplet photosensitisers for the cross-linking [2 + 2] cycloaddition [7]. The liquid mixture **10f–i** was selected for development and is now being used commercially in an offset printing plate system [8].

When the phenoxy derivative **6o** is irradiated with UV light in solution or in a polymer matrix a blue coloration is observed. This interesting effect shall be discussed in a forthcoming paper.

4. Conclusions. – The scope of thioxanthone and xanthone photosensitisers and photoinitiators is considerably extended by the introduction of imide and vicinal dialkyldicarboxylate functions. Large bathochromic shifts (up to 74 nm compared to the parent compound) can be reached. By further elaboration of the functional groups, a wide range of solubility properties tailor-made for special applications can be designed. A liquid isomeric mixture of dioctyl oxothioxanthene-3,4-dicarboxylates was successfully introduced to the market.

The technical assistance of Miss *K. Fluri*, Miss *G. Disler*, and Miss *Ch. Helbling* is gratefully acknowledged.

Experimental Part

General. See [3]. The disodium salts of thiosalicylic and salicylic acids were prepared by dissolving the acids in 2.00 equiv. of 1N NaOH in H_2O and evaporating to dryness, at the end twice with xylene (azeotropes). UV spectra: generally in $CHCl_3$; only the absorption with longest wavelength is given; λ_{max} in nm (ε_{max}).

3-Nitrophthalimide (**1a**) is commercially available (*Lancaster Synthesis Ltd.*).

N-*Methyl-3-nitrophthalimide* (**1b**) [9] *and 4,5-Dichloro-* N-*methylphthalimide* (**4b**) [10] were prepared by known procedures.

N-*Butyl-3,5-dinitrophthalimide* (**1c**). A mixture of 3,5-dinitrophthalic anhydride [11] (23.81 g, 100 mmol), $BuNH_2$ (7.31 g, 100 mmol), and xylene (150 ml) was stirred mechanically at 105° for 10 min. The mixture was gradually heated and refluxed (H_2O being distilled off) for 30 min, cooled slowly to 70°, and filtered to remove some small amounts of 3,5-dinitrophthalic acid. The filtrate was evaporated and the residue recrystallised from CH_2Cl_2/Et_2O/pentane: 27.53 g (94%) of **1c**. M.p. 40–42°. ^{1}H-NMR ($CDCl_3$): 8.90, 8.79 (2*d*, J = 1.5, H–C(4), H–C(6)); 3.78 (2*t*, J = 8, CH_2N); 2.0–1.2 (4*m*, CH_2CH_2); 1.00 (3*t*, J = 8, CH_3). Anal. calc. for $C_{12}H_{11}N_3O_6$ (293.24): C 49.15, H 3.78, N 14.33; found: C 49.46, H 3.89, N 14.35.

*2-[(2,3-Dihydro-1,3-dioxo-1*H*-isoindol-4-yl)thio]benzoic Acid* (**2a**). A mixture of **1a** (40 g, 208.2 mmol), thiosalicylic acid disodium salt (49.49 g, 249.8 mmol), and *N,N*-dimethylformamide (DMF; 200 ml) was stirred at 80° for 8 h. The mixture was evaporated at 70° and the residue stirred with 2N HCl. The precipitate was filtered, washed with H_2O, dried, and recrystallised from dioxane: 50.2 g (81%) of **2a**. M.p. 289–290°. Anal. calc. for $C_{15}H_9NO_4S$ (299.3): C 60.19, H 3.03, N 4.67, O 21.38, S 10.71; found: C 59.55, H 3.16, N 4.57, O 21.49, S 10.46.

*2-[(2,3-Dihydro-2-methyl-1,3-dioxo-1*H*-isoindol-4-yl)thio]benzoic Acid* (**2b**). A mixture of **1b** [9] (15 g, 72.7 mmol), thiosalicylic acid disodium salt (18.1 g, 91 mmol), and tetrahydrofuran (THF; 750 ml) were refluxed for 1 d. When cold, the mixture was treated with toluene and 2N HCl. The org. extracts were dried (Na_2SO_4) and evaporated. Recrystallisation from dioxane gave 15.54 g (68%) of **2b**. M.p. 270–272°. Anal. calc. for $C_{16}H_{11}NO_4S$ (313.33): C 61.34, H 3.54, N 4.47, S 10.23; found: C 61.00, H 3.60, N 4.80, S 9.90.

*2-[(2-Butyl-2,3-dihydro-6-nitro-1,3-dioxo-1*H*-isoindol-4-yl)thio]benzoic Acid* (**2c**). A mixture of **1c** (1.47 g, 5 mmol), thiosalicylic acid disodium salt (1.24 g, 6 mmol), and THF (15 ml) was refluxed for 5 h. THF (15 ml), toluene (30 ml), and 2N HCl (10 ml) were added. The org. phase was separated, washed with brine, dried, and evaporated. Recrystallisation from THF/toluene gave 1.80 g (90%) of **2c**. M.p. 192–196°. Anal. calc. for $C_{19}H_{16}N_2O_6S$ (400.41): C 57.00, H 4.03, N 7.00, S 8.01; found: C 56.82, H 4.10, N 6.95, S 7.72.

*2-{[2-Butyl-6-(decylthio)-2,3-dihydro-1,3-dioxo-1*H*-isoindol-4-yl]thio}benzoic Acid* (**2d**). At 25°, **2c** (20 g, 49.9 mmol), decanethiol (9.08 g, 54.9 mmol), K_2CO_3 (27.6 g, 199.6 mmol), and DMF (500 ml) were stirred for 2 h. The mixture was evaporated and the residue dissolved in CH_2Cl_2/2N HCl. The org. extracts were washed with brine, dried (Na_2SO_4), and evaporated. Recrystallisation from cyclohexane gave 27.56 g (93%) of **2d**. M.p. 113–115°. Anal. calc. for $C_{29}H_{35}NO_4S_2$ (525.72): C 66.26, H 6.71, N 2.66, S 12.15, O 12.13; found: C 66.23, H 7.01, N 2.70, S 12.09, O 11.97.

*2-{[2-Butyl-2,3-dihydro-1,3-dioxo-6-(phenylthio)-1*H*-isoindol-4-yl]thio}benzoic Acid* (**2e**). Analogously to **2d**, with **2c** (12.81 g, 32 mmol), thiophenol (3.88 g, 35.2 mmol), K_2CO_3 (13.27 g, 96 mmol), and DMF (120 ml). Recrystallisation from toluene/cyclohexane gave 13.52 g (91%) of **2e**. M.p. 154–156°. Anal. calc. for $C_{25}H_{21}NO_4S_2$ (463.57): C 64.77, H 4.57, N 3.02, S 12.83; found: C 64.96, H 4.73, N 3.20, S 13.62.

N-*Benzyl-4-chlorophthalimide* (**4a**). A mixture of 4-chlorophthalic anhydride (13 g, 71.2 mmol), benzylamine (7.63 g, 71.2 mmol), and xylene (130 ml) was refluxed with azeotropic removal of H_2O. The mixture was evaporated and the residue recrystallised from toluene/cyclohexane: 18.01 g (93%) of **4a**. M.p. 117–119°. Anal. calc. for $C_{15}H_{10}ClNO_2$ (271.70): C 66.31, H 3.71, N 5.16, Cl 13.05; found: C 65.90, H 3.80, N 5.40, Cl 13.00.

*10-Oxo-10*H*-dibenzo[b,e]thiopyran-3,4-dicarboximide* (**6a**). A suspension of **2a** (20 g, 66.8 mmol) in polyphosphoric acid (PPA; 130 g) was stirred at 150° for 90 min. The mixture was cooled and added to H_2O (500 ml) with stirring. The precipitate was filtered, washed several times with H_2O, and dried *in vacuo*. Recrystallisation from xylene gave 12.4 g (66%) of **6a**. M.p. 348–350°. UV: 420 (5200). Anal. calc. for $C_{15}H_7NO_3S$ (281.29): C 64.05, H 2.51, N 4.98, O 17.06, S 11.40; found: C 63.87, H 2.79, N 4.98, O 17.17, S 11.25.

N-*Methyl-10-oxo-10*H*-dibenzo[b,e]thiopyran-3,4-dicarboximide* (**6b**). Imide **2b** (15.5 g, 49.5 mmol) was converted to the acyl chloride by refluxing in THF (400 ml) and oxalyl chloride (150 ml) for 5 h. Chlorobenzene (150 ml) was added. The mixture was evaporated to a total volume of 150 ml, and $AlCl_3$ (13.2 g, 98.9 mmol) was added. Then the mixture was stirred at 25° for 18 h and evaporated, the residue dissolved in 2N HCl/THF/toluene, and the org. phase washed with sat. aq. $NaHCO_3$ soln., dried (Na_2SO_4), and evaporated. Recrystallisation from dioxane gave 5 g (34%) of **6b**. M.p. 287–288°. UV: 420 (4800). Anal. calc. for $C_{16}H_9NO_3S$ (295.31): C 65.08, H 3.07, N 4.74, S 10.86; found: C 65.03, H 3.16, N 4.75, S 10.65.

N-Butyl-1-nitro-10-oxo-10H-dibenzo[b,e]thiopyran-3,4-dicarboximide (**6c**). For 3 h, **2c** (20 g, 50 mmol) was stirred with PPA (80 g) at 180°. The mixture was stirred with H_2O (300 ml) and the precipitate filtered, washed with H_2O, and dried. Recrystallisation from toluene gave 12.3 g (64%) of **6c**. M.p. 264–266°. UV: 430 (br., 3800). Anal. calc. for $C_{19}H_{14}N_2O_5S$ (382.39): C 59.67, H 3.69, N 7.33, O 20.92, S 8.38; found: C 59.76, H 3.86, N 7.36, O 20.84, S 8.19.

N-Butyl-1-(decylthio)-10-oxo-10H-dibenzo[b,e]thiopyran-3,4-dicarboximide (**6d**). Imide **2d** (11.01 g, 21.7 mmol) was converted to the acyl chloride and reacted with $AlCl_3$ similarly to **6b** to give, after recrystallisation from cyclohexane, 10.34 g, (95%) of **6d**. M.p. 143–145°. UV: 456 (8600). ^{1}H-NMR ($CDCl_3$): 8.42 (*dd*, J = 1.5, 8, H–C(9)); 7.8–7.4 (3*m*, H–C(6), H–C(7), H–C(8)); 7.54 (*s*, H–C(2)); 3.77 (2*t*, J = 9, CH_2N); 2.94 (2*t*, J = 9, CH_2S); 1.9–0.8 (26*m*, CH_2, CH_3). Anal. calc. for $C_{29}H_{35}NO_3S_3$ (509.72): C 68.33, H 6.92, N 2.75, S 12.58; found: C 68.30, H 6.88, N 2.76, S 12.28.

N-Butyl-10-oxo-1-(phenylthio)-10H-dibenzo[b,e]thiopyran-3,4-dicarboximide (**6e**). Similarly to **6d**, **2e** (12.51 g, 27 mmol) was cyclised to give, after recrystallisation from toluene, 11.1 g (92%) of **6e**. M.p. 265–268°. UV: 453 (9800). ^{1}H-NMR ($CDCl_3$): 8.58 (*dd*, J = 2, 9, H–C(9)); 7.7–7.4 (8*m*, H–C(6), H–C(7), H–C(8), PhS); 7.17 (*s*, H–C(2)); 3.73 (2*t*, J = 8, CH_2N); 1.8–1.2 (4*m*, CH_2CH_2); 0.96 (3*t*, J = 7, CH_3). Anal. calc. for $C_{25}H_{19}NO_3S_2$ (445.55): C 67.39, H 4.30, N 3.14, S 14.39; found: C 67.28, H 4.29, N 3.16, S 14.13.

N-Octyl-10-oxo-10H-dibenzo[b,e]thiopyran-3,4-dicarboximide (**6f**). At 80°, **6a** (4 g, 14.2 mmol), octyl bromide (4.12 g, 21.3 mmol), K_2CO_3 (5.89 g, 42.7 mmol), and DMF (40 ml) were stirred for 1 d. The mixture was evaporated and the residue dissolved in 2N HCl/CH_2Cl_2. The org. phase was washed with sat. $NaHCO_3$ soln. and brine, dried, and evaporated. Recrystallisation from cyclohexane gave 5.28 g (95%) of **6f**. M.p. 188–190°. UV: 420 (4800). ^{1}H-NMR ($CDCl_3$): 8.89 (*d*, J = 8, H–C(1)); 8.56 (*dd*, J = 1, 9, H–C(9)); 7.81 (*d*, J = 8, H–C(2)); 7.7–7.4 (3*m*, H–C(6), H–C(7), H–C(8)); 3.72 (2*t*, J = 8, CH_2N); 1.78 (2*m*, CH_2CH_2N); 1.6–1.15 (10*m*, CH_2); 0.92 (3*t*, J = 7, CH_3). Anal. calc. for $C_{23}H_{23}NO_3S$ (393.50): C 70.20, H 5.89, N 3.56, O 12.20, S 8.15; found: C 70.05, H 5.86, N 3.71, O 12.77, S 8.11.

N-Benzyl-10-oxo-10H-dibenzo[b,e]thiopyran-1,2-dicarboximide (**7a**) *and N-Benzyl-10-oxo-10H-dibenzo[b,e]thiopyran-2,3-dicarboximide* (**8**). A mixture of **4a** (1 g, 3.7 mmol), thiosalicylic acid disodium salt (1.46 g), and DMF (10 ml) was stirred at reflux for 4 h. The mixture was evaporated and the residue suspended in $NaHCO_3$ soln. This mixture was extracted with THF/toluene. The aq. phase was acidified (2N HCl) and extracted with THF/toluene. The org. extracts were evaporated to give crude *2-[(2-benzyl-2,3-dihydro-1,3-dioxo-1H-isoindol-5-yl)thio]benzoic acid* (**3a**) which was stirred with PPA (14.8 g) at 200° for 30 min. The mixture was stirred with H_2O adjusted to pH 8–9 and the precipitate collected and dried. Chromatography (silica gel, CH_2Cl_2) gave first 0.12 g (9%) of **8**. M.p. 289–294°. UV: 407 (4800). ^{1}H-NMR ($(CD_3)_2SO$): 9.27 (*s*, H–C(1)); 9.08 (*m*, H–C(9)); 8.99 (*s*, H–C(4)); 8.6–8.3 (3*m*, H–C(6), H–C(7), H–C(8)); 8.11 (5*m*, Ph); 5.62 (2*s*, CH_2). Anal. calc. for $C_{22}H_{13}NO_3S$ (371.41): C 71.15, H 3.53, N 3.77; found: C 71.62, H 3.91, N 3.60.

A second fraction gave 0.04 g (3%) of **7a**. M.p. 210–213°. UV: 405 (3000). ^{1}H-NMR ($CDCl_3$): 8.51 (*m*, H–C(9)); 7.95 (*d*, J = 7, H–C(3)); 7.77 (*d*, J = 7, H–C(4)); 7.65–7.2 (8*m*, Ph, H–C(5), H–C(6), H–C(7)); 4.90 (2*s*, CH_2). Anal. found: C 70.78, H 4.17, N 3.66.

4-Chloro-N-methyl-10-oxo-10H-dibenzo[b,e]thiopyran-1,2-dicarboximide (**7b**). A mixture of **4b** (2.3 g, 10 mmol), thiosalicylic acid disodium salt (2.69 g, 13 mmol), and DMF (12 ml) was stirred at 80° for 18 h. The mixture was dissolved in 2N HCl/THF/toluene. The org. phase was separated and extracted with $NaHCO_3$ soln. The basic aq. extracts were acidified and extracted with THF/toluene. The org. phases were dried and evaporated. Recrystallisation from THF/toluene gave 1.1 g (32%) of crude *2-[(6-chloro-2,3-dihydro-2-methyl-1,3-dioxo-1H-isoindol-5-yl)thio]benzoic acid* (**3b**). This was heated in PPA (12 g) at 200° for 10 min. The mixture was stirred with H_2O and extracted with THF/toluene. The org. extracts were washed with $NaHCO_3$ soln. and brine, dried (Na_2SO_4), and evaporated. Recrystallisation from THF/toluene gave 0.58 g (55% based on **3b**) of **7b**. M.p. 258–266°. UV: 399 (br., 3400). ^{1}H-NMR ($CDCl_3$): 8.41 (*m*, H–C(9)); 8.00 (*s*, H–C(3)); 7.7–7.4 (3*m*, H–C(6), H–C(7), H–C(8)); 3.24 (3*s*, CH_3). Anal. calc. for $C_{16}H_8ClNO_3S$ (329.76): C 58.28, H 2.45, H 4.25; found: C 58.53, H 2.74, N 4.32.

N-Methyl-9-oxo-9H-xanthene-3,4-dicarboximide (**9**). A mixture of **1b** (1.65 g, 8 mmol), salicylic acid disodium salt (1.6 g, 8.7 mmol), and *N,N*-dimethylacetamide (10 ml) was stirred at 120° for 30 min. The mixture was dissolved in 2N HCl/THF/toluene. The org. phase was extracted with $NaHCO_3$ soln. The basic aq. extracts were acidified and extracted with THF/toluene. The extracts were dried and evaporated with simultaneous sublimation of the excess of salicylic acid to give 1.57 g of crude *2-[(2,3-dihydro-2-methyl-1,3-dioxo-1H-isoindol-4-yl)-oxy]benzoic acid* (**5**). This was heated with PPA (14 g) at 150° for 90 min. The mixture was stirred with H_2O and extracted with THF/toluene after basification to pH 10. The extracts were washed with $NaHCO_3$ soln. and brine, dried, and evaporated. Recrystallisation from THF gave 0.34 g (23%) of **9**. M.p. 280–283°. UV: 372 (6600). Anal. calc. for $C_{16}H_9NO_4$: C 68.82, H 3.25, N 5.02; found: C 68.62, H 3.04, N 5.22.

10-Oxo-10H-dibenzo[b,e]thiopyran-3,4-dicarboxylic Anhydride (**11**). For 90 min, **6a** (4.8 g, 17.1 mmol) was refluxed with 0.1N NaOH (511 ml). The mixture was acidified with conc. HCl soln. and refluxed for 18 h. The crude diacid **10a** was filtered, washed with H_2O dried, and dehydrated by refluxing with Ac_2O (11 ml) in xylene (100 ml). Partial evaporation, cooling, and filtration gave 4.32 g (90%) of **11**. M.p. 330–331°. UV: 423 (4900). ^{1}H-NMR ($CDCl_3$): 9.16 (*d*, $J = 7$, H–C(1)); 8.67 (*m*, H–C(9)); 8.05 (*d*, $J = 7$, H–C(2)); 7.8–7.55 (3*m*, H–C(6), H–C(7), H–C(8)). Anal. calc. for $C_{15}H_6O_4S$ (282.27): C 63.83, H 2.14, O 22.67, S 11.36; found: C 63.97, H 2.01, O 22.61, S 11.13.

Disodium 10-Oxo-10H-dibenzo[b,e]thiopyran-3,4-dicarboxylate (**10b**). Anhydride **11** (30 g, 106 mmol) and 2.00N NaOH (265.7 ml) were refluxed for 45 min (→ clear soln.). The soln. was cooled with stirring to 25°. The precipitate was filtered, washed with EtOH, and recrystallised from EtOH/H_2O to give **10b** · ½ H_2O quantitatively. M.p. > 350°. UV (H_2O): 394 (5500). ^{1}H-NMR (D_2O): 8.54 (*d*, $J = 9$, H–C(1)); 8.26 (*m*, H–C(9)); 7.87 (*d*, $J = 9$, H–C(2)); 7.8–7.25 (3*m*, H–C(6), H–C(7), H–C(8)). Anal. calc. for $C_{15}H_6Na_2SO_5 \cdot 0.5\ H_2O$ (353.25): C 51.00, H 1.99, Na 13.00, S 9.07; found: C 50.87, H 2.11, Na 12.95, S 8.96.

3-Ethyl Hydrogen 10-Oxo-10H-dibenzo[b,e]thiopyran-3,4-dicarboxylate (**10c**). A mixture of **11** (1 g, 3.5 mmol) and EtOH (20 ml) was refluxed for 3 h and then evaporated at 60°. The residue was dissolved in CH_2Cl_2 and the soln. washed with 2N HCl, dried, and evaporated. ^{1}H-NMR: **10c**/**10d** *ca.* 3:1. Recrystallisation from CH_2Cl_2/pentane gave 0.79 g (68%) of pure **10c**. M.p. 315–319°. UV: 395 (5600). ^{1}H-NMR ($CDCl_3$): 8.81 (*d*, $J = 8$, H–C(1)); 8.63 (*m*, H–C(9)); 8.00 (*d*, $J = 8$, H–C(2)); 7.8–7.5 (3*m*, H–C(6), H–C(7), H–C(8)); 4.49 (2*q*, $J = 7$, CH_2); 1.46 (3*t*, $J = 7$, CH_3). Anal. calc. for $C_{17}H_{12}O_5S$ (328.34): C 62.19, H 3.69, O 24.37, S 9.77; found: C 61.82, H 3.77, O 24.48, S 9.69.

Dibutyl 10-Oxo-10H-dibenzo[b,e]thiopyran-3,4-dicarboxylate (**10e**). A mixture of **11** (2.9 g, 10.3 mmol), BuOH (58 ml), toluene (15 ml), and 96% H_2SO_4 (0.87 ml) was refluxed with azeotropic removal of H_2O in a *Dean-Stark* trap for 20 h. The mixture was partly evaporated and dissolved in H_2O/CH_2Cl_2. The org. extracts were washed with brine, dried, and evaporated at 150° *in vacuo* to give 3.92 g (92%) of **10e**. M.p. 49–51°. UV: 397 (6080). ^{1}H-NMR ($CDCl_3$): 8.74 (*d*, $J = 9$, H–C(1)); 8.55 (*m*, H–C(9)); 7.95 (*d*, $J = 9$, H–C(2)); 7.6–7.3 (3*m*, H–C(6), H–C(7), H–C(8)); 4.43, 4.39 (4*qq*, $J = 7$, 7, CH_2O); 2.0–1.3 (8*m*, CH_2CH_2); 1.03 (6*m*, CH_3). Anal. calc. for $C_{23}H_{24}O_5S$ (412.50): C 66.97, H 5.86, O 19.39, S 7.77; found: C 67.10, H 5.88, O 19.14, S 7.63.

Mixture **10f–i** *of Isomeric Dioctyl 10-Oxo-10H-dibenzo[b,e]thiopyran-3,4-dicarboxylates.* Anhydride **11** (50.5 g, 179 mmol), octanol (100 ml), and 2-ethylhexanol (100 ml) were refluxed for 2 h. Then, 96% H_2SO_4 (0.15 g) was added and reflux continued for further 12 h. The mixture was evaporated at 150° *in vacuo* and the residue dissolved in CH_2Cl_2. The suspension was filtered over silica gel (170 g) and the filtrate evaporated to give 71.26 g (76%) of a liquid mixture of **10f–i**. UV: 394 (5700). Anal. calc. for $C_{31}H_{40}O_5S$ (524.72): C 70.96, H 7.68, S 6.11; found: C 71.14, H 7.55, S 6.05.

N-(2-Ethylhexyl)-10-oxo-10H-dibenzo[b,e]thiopyran-3,4-dicarboximide (**6g**). Anhydride **11** (2 g, 7.1 mmol), 2-ethylhexylamine (0.92 g, 7.1 mmol), and xylene (20 ml) were refluxed with azeotropic removal of H_2O for 30 min. Cooling and filtration gave 2.35 g (85%) of **6g**. M.p. 189–190°. UV: 420 (4600). Anal. calc. for $C_{23}H_{23}NO_3S$ (393.50): C 70.20, H 5.89, N 3.56, S 8.15; found: C 70.05, H 5.57, H 3.54, S 8.17.

Similarly prepared were the following derivatives:

10-Oxo-N-[2-(sodiosulfonato)ethyl]-10H-dibenzo[b,e]thiopyran-3,4-dicarboximide (**6h**). Yield 84%. M.p. > 330° (recrystallised from H_2O/THF). UV (H_2O): 424 (4700). Anal. calc. for $C_{17}H_{10}NNaO_6S_2$ (411.38): C 49.64, H 2.45, N 3.41, Na 5.59, S 15.59; found: C 49.85, H 2.71, N 3.79, Na 5.48, S 15.56.

N-[2-(Diethylamino)ethyl]-10-oxo-10H-dibenzo[b,e]thiopyran-3,4-dicarboximide (**6i**). Yield 81%. M.p. 174–176° (from dioxane). UV: 419 (4500). Anal. calc. for $C_{21}H_{20}N_2O_3S$ (380.46): C 66.29, H 5.30, N 7.36, O 12.61, S 8.42; found: C 66.39, H 5.43, N 7.48, O 12.67, S 8.21.

N-Allyl-10-oxo-10H-dibenzo[b,e]thiopyran-3,4-dicarboximide (**6k**). Yield 75%. M.p. 242–244°. UV: 420 (4800). Anal. calc. for $C_{18}H_{11}NO_3S$ (321.35): C 67.28, H 3.45, N 4.36, O 14.94, S 9.98; found: C 66.91, H 3.65, N 4.09, O 15.28, S 9.99.

N-(2-Hydroxyethyl)-10-oxo-10H-dibenzo[b,e]thiopyran-3,4-dicarboximide (**6l**). Yield 82%. M.p. 287–289° (from dioxane). UV: 420 (4800). Anal. calc. for $C_{17}H_{11}NO_4S$ (325.34): C 62.76, H 3.41, N 4.31, S 9.86; found: C 62.24, H 3.38, N 4.28, S 9.58.

10-Oxo-N-(4-tolyl)-10H-dibenzo[b,e]thiopyran-3,4-dicarboximide (**6m**). Yield 92%. M.p. 296–299° (from dioxane). UV: 419 (5000). Anal. calc. for $C_{22}H_{13}NO_3S$ (371.41): C 71.15, H 3.53, N 3.77, S 8.63; found: C 71.08, H 3.61, N 3.62, S 8.63.

N-Butyl-1-hydroxy-10-oxo-10H-dibenzo[b,e]thiopyran-3,4-dicarboximide (**6n**). At 50°, **6c** (3 g, 7.8 mmol), K_2CO_3 (2.2 g, 15.9 mmol), and DMF (35 ml) were stirred for 1 h. The mixture was evaporated and the residue dissolved in 2N HCl/THF/toluene. The org. extracts were dried and evaporated. Recrystallisation from THF gave

2.04 g (74%) of **6n**. M.p. 191–193°. UV: 440 (5200). ^{1}H-NMR ($CDCl_3$): 8.54 (*m*, H–C(9)); 7.8–7.4 (3*m*, H–C(6), H–C(7), H–C(8)); 7.19 (*s*, H–C(2)); 3.66 (2*t*, J = 7, CH_2N); 1.9–1.2 (4*m*, CH_2CH_2); 0.97 (3*m*, CH_3). Anal. calc. for $C_{19}H_{15}NO_4S$ (353.39): C 64.58, H 4.28, N 3.97, S 9.07; found: C 64.29, H 4.39, N 3.85, S 8.83.

*N-Butyl-10-oxo-1-(phenyloxy)-10*H*-dibenzo[*b,e*]thiopyran-3,4-dicarboximide* (**6o**). At 25°, **6c** (3 g, 7.85 mmol), phenol (0.89 g, 9.41 mmol), K_2CO_3 (2.16 g, 15.69 mmol), and DMSO (50 ml) were stirred for 2 h. The mixture was treated with 2N HCl (200 ml); the precipitate collected and dissolved in CH_2Cl_2, and the soln. dried (Na_2SO_4) and evaporated. Recrystallisation from CH_2Cl_2/pentane gave 2.88 g (86%) of **6o**. M.p. 198–199°. UV: 417 (5360); photosensitive in soln. to give a blue colour. Anal. calc. for $C_{25}H_{19}NO_4S$ (429.49): C 69.91, H 4.46, N 3.26, O 14.90, S 7.47; found: C 69.72, H 4.52, N 3.48, O 15.01, S 7.39.

*N-Butyl[2]benzothiopyrano[4,3,2-*cd*][2,1]benzisoxazole-4,5-dicarboximide* (**12**). Imide **6c** (1 g, 2.61 mmol), NaN_3 (0.34 g, 5.23 mmol), and DMF (10 ml) were stirred at 25° for 90 min (evolution of N_2). The mixture was stirred with H_2O, the precipitate collected, washed with H_2O, dried, and dissolved in CH_2Cl_2, and the soln. dried (Na_2SO_4) and evaporated. Recrystallisation from CH_2Cl_2 gave 0.75 g (82%) of **12**. M.p. 211–213°. UV: 450 (11000), 427 (12900). ^{1}H-NMR ($CDCl_3$): 8.11 (*m*, H–C(10)); 7.7–7.4 (4*m*, H–C(3) (*s*), H–C(7), H–C(8), H–C(9)); 3.68 (2*t*, J = 8, CH_2N); 1.9–1.2 (4*m*, CH_2CH_2); 0.98 (3*m*, CH_3). Anal. calc. for $C_{19}H_{14}N_2O_3S$ (350.39): C 65.13, H 4.03, N 8.00, S 9.15; found: C 65.23, H 4.28, N 8.06, S 8.95.

REFERENCES

[1] W. Fischer, V. Kvita, *Helv. Chim. Acta* **1985**, *68*, 854.

[2] a) M. J. Davis, J. Doherty, A. A. Godfrey, P. N. Green, J. R. A. Joung, M. A. Parrish, *J. Oil Col. Chem. Assoc.* **1978**, *61*, 256; b) K. Meier, H. Zweifel, *J. Photochem.* **1986**, *35*, 353; c) J. P. Fouassier, D. J. Lougnot, A. Paverne, F. Wieder, *Chem. Phys. Lett.* **1987**, *135*, 30; d) N. S. Allen, F. Catalina, B. Moghaddam, P. N. Green, W. A. Green, *Eur. Polym. J.* **1986**, *22*, 691; e) W. Rutsch, G. Berner, R. Kirchmayr, R. Hüsler, G. Rist, N. Bühler, *Org. Coat.* **1986**, *8*, 175.

[3] W. Fischer, V. Kvita, *Helv. Chim. Acta* **1985**, *68*, 846.

[4] F. Benedetti, D. R. Marshall, C. J. M. Stirling, J. L. Leng, *J. Chem. Soc., Chem. Commun.* **1982**, 918.

[5] a) A. Schaarschmidt, *Ber. Dtsch. Chem. Ges.* **1916**, *49*, 1632; b) L. Gattermann, R. Ebert, *ibid.* **1916**, *49*, 2117; c) L. Gattermann, H. Rolfes, *Liebigs Ann. Chem.* **1921**, *425*, 135.

[6] N. Baumann, H. Zweifel, M. Baumann, J. S. Waterhouse, to *Ciba-Geigy Corp.*, 1978, US. Pat. 4.079.041.

[7] W. Fischer, J. Finter, H. Zweifel, to *Ciba-Geigy AG*, 1983, EP 110832; US Pat. 4.585.876.

[8] IRGAPLATE™ System; photosensitizer: IRGAPLATE™ XSE 1003 (*Ciba-Geigy AG*).

[9] R. Dabard, J. Tirouflet, *Bull. Soc. Chim. Fr.* **1957**, 565.

[10] P. H. Mazzocchi, P. Wilson, F. Khachik, L. Klingler, S. Minamikawa, *J. Org. Chem.* **1983**, *48*, 2981.

[11] R. Eder, C. Widmer, *Helv. Chim. Acta* **1923**, *6*, 966.