93. Aromatic Nucleophilic Substitution

Part 2[1])

Preparation of Novel 3-Substituted Xanthone and Thioxanthone Derivatives[2])

by **Walter Fischer*** and **Vratislav Kvita**

Central Research Laboratories, *Ciba-Geigy AG*, CH-4002 Basle

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The novel 3-nitro-9-oxo-9*H*-xanthene- and 3-nitro-9-oxo-9*H*-thioxanthene-1-carboxylic acids **2a–d** were prepared by intramolecular acylation of 3-aryloxy- and 3-arylthio-5-nitrophthalic anhydrides **1** *(Scheme)*. The 3-nitro group was readily substituted by O- and S-nucleophiles and halide and azide ions to give a range of 3-substituted thioxanthone derivatives **3** with varied λ_{max}.

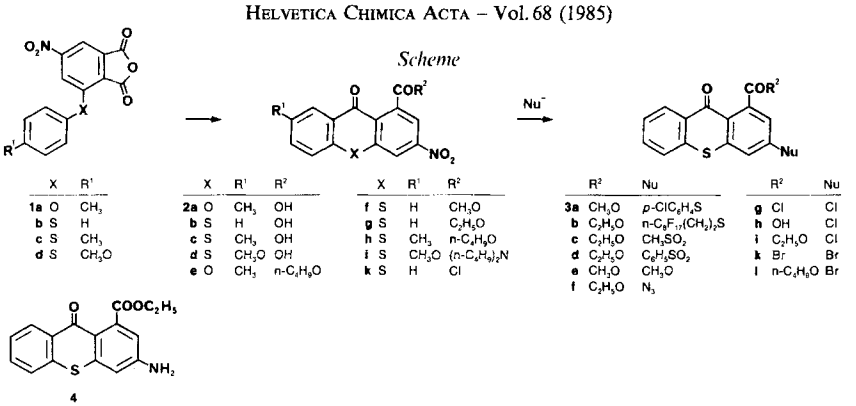
1. Introduction. – Photopolymerisation and photocrosslinking reactions of unsaturated compounds find growing interest in modern industrial applications [2]. Due to their favourable UV/VIS spectra, xanthones and thioxanthones are especially useful photoinitiators for white pigmented resin formulations [3]. Furthermore, they are able to sensitize the [2 + 2]-photo-cycloaddition of dimethylmaleinimide derivatives, a reaction which has been used to photocrosslink polymers [4]. We recently found a new access to 9-oxo-9*H*-thioxanthene-1-carboxylic acid derivatives by intramolecular cyclization of 3-(phenylthio)phthalic-acid or -anhydride derivatives [5]. For special applications, it was necessary to prepare xanthones and thioxanthones with suitable substituents to obtain hypsochromic or, more important, bathochromic shifts in order to adjust the absorption wavelengths as close as possible to the emission wavelengths of the commonly used UV lamps. In the preceding paper [1] we described the synthesis of the novel 5-nitro-3-tolyloxy- and 5-nitro-3-(phenylthio)phthalic-acid derivatives **1a–d**. We now report their conversion to the corresponding 3-nitro-9-oxo-9*H*-xanthene- and 3-nitro-9-oxo-9*H*-thioxanthene-1-carboxylic acids **2a–d** and further transformations of these derivatives by nucleophilic substitution of the 3-nitro group.

2. Syntheses. – a) *Preparation of 3-Nitro-9-oxo-9*H*-xanthene- and 3-Nitro-9-oxo-9*H*-thioxanthene-1-carboxylic Acids* **2a–d**, *their Esters* **2e–h**, *and Amide* **2i**. The phthalic anhydrides **1** were cyclized by intramolecular acylation with $AlCl_3$ in 1,1,2,2-tetrachloroethane at elevated temperatures. The anhydrides **1a–c** required 2.5 equiv. of $AlCl_3$ for complete reaction (obviously the products are complexed by 2 equiv. of $AlCl_3$) and gave good yields of **2a–c**. The methoxy derivative **1d** required at least 3 equiv. of $AlCl_3$, and the yield was low, probably due to a considerable amount of ether cleavage. As expected

[1]) Part 1: see [1].

[2]) Presented in part at the Herbstversammlung der Schweizerischen Chemischen Gesellschaft, Berne, October, 1981.

Scheme



	X	R¹
1a	O	CH_3
b	S	H
c	S	CH_3
d	S	CH_3O

	X	R¹	R²
2a	O	CH_3	OH
b	S	H	OH
c	S	CH_3	OH
d	S	CH_3O	OH
e	O	CH_3	n-C_4H_9O

	X	R¹	R²
f	S	H	CH_3O
g	S	H	C_2H_5O
h	S	CH_3	n-C_4H_9O
i	S	CH_3O	$(n\text{-}C_4H_9)_2N$
k	S	H	Cl

	R²	Nu
3a	CH_3O	p-ClC_6H_4S
b	C_2H_5O	n-$C_8F_{17}(CH_2)_2S$
c	C_2H_5O	CH_3SO_2
d	C_2H_5O	$C_6H_5SO_2$
e	CH_3O	CH_3O
f	C_2H_5O	N_3

	R²	Nu
g	Cl	Cl
h	OH	Cl
i	C_2H_5O	Cl
k	Br	Br
l	n-C_4H_9O	Br

4

from the electron density in the aromatic ring, the xanthone derivative **2a** was formed under milder conditions than the thioxanthone derivative **2c**.

Alternatively, **2b** could be prepared directly from 5-nitro-3-(phenylthio)phthalic acid by heating with an excess of polyphosphoric acid [4]. The anhydride **1b** was probably formed as an intermediate. The pure anhydrides **1a–c** were not sufficiently soluble in polyphosphoric acid and tended to give low yields of **2a–c** due to sublimation or decomposition at the high reaction temperature (200°). The methoxy compound **1d** decomposed completely under these conditions.

The esters **2e–h** and the amide **2i** were prepared in the usual way (see *Exper. Part*).

b) *Reduction.* The nitro ester **2g** was hydrogenated to give the amine **4** in quantitative yield.

c) *Nucleophilic Substitutions of the 3-Nitro Groups.* The nucleophilic substitution of aromatic nitro groups has attracted increasing attention in recent years [6]. The nitro groups in 4-nitrobenzophenone and 1- and 3-nitroxanthone were substituted by alkoxides [7]. Other nucleophilic substitutions with 4-nitrobenzophenone were also reported [8] [9]. We have now extended these reactions to the above-mentioned 3-nitro-9-oxo-9*H*-thioxanthenecarboxylic-acid derivatives.

Reaction of the nitro esters **2f,g** with potassium thiolates (prepared *in situ* with K_2CO_3 in DMF) to give **3a,b**, of **2g** with sodium methanesulfinate and sodium benzenesulfinate to give **3c,d**, and of **2f** with $NaOCH_3$ to give **3e** proceeded under mild conditions in good to excellent yields.

Reaction of **2g** with NaN_3 in DMF gave the azide **3f** in quantitative yield. It proved to be stable at room temperature in the dark but decomposed slowly in daylight.

With refluxing $SOCl_2$, the nitro acid **2b** reacted quickly to the corresponding nitro-acyl chloride **2k**. On further heating, **2k** gave, in a slower substitution reaction, the corresponding chloro-acyl chloride **3g**. With H_2O, the acid **3h** was formed from **3g**, whereas EtOH gave the ethyl ester **3i**. Similar substitutions of nitro groups by chloride ion are known from the literature [10]. The reaction **2k**→**3g** also took place with $POCl_3$ and PCl_5 [10b], but not with oxalyl chloride. Thus, the latter reagent could be used to prepare the nitro-acyl chloride **2k** without additional halogenation. Surprisingly, the nitro esters **2f,g** did not react with $SOCl_2$ under these conditions. Obviously the stronger electron-withdrawing effect of the COCl group (compared to the COOR group) is essential for this reaction. Even the 7-methyl group of the acid **2c** deactivates the nitro group sufficiently to suppress the substitution reaction completely under the same condi-

tions. $POBr_3$ is not stable enough to give a similar substitution reaction, but with PBr_3 the corresponding bromo-acyl bromide **3k** was formed *in situ*. It reacted with BuOH to give the bromo ester **3l** in low yield (for similar substitutions of nitro groups by bromide ion, see [10c] [10d]).

3. Conclusions. – As can be seen from these results, the nitro groups in the 3-nitro-9-oxo-9*H*-thioxanthene-1-carboxylic-acid derivatives are highly reactive towards a variety of nucleophiles. An important factor that contributes to this reactivity is the coplanarity of the carbonyl group and the two benzene rings enforced by the S-bridge. This effect also explains the higher reactivity of 3-nitroxanthone *versus* 4-nitrobenzophenone [7].

The UV spectra (see *Exper. Part*) reveal that these new photosensitizers **2–4** show the expected hypsochromic or bathochromic shifts compared to unsubstituted thioxanthone (382 nm) over a relatively wide range (332 nm for the amino compound **4**, 436 nm for nitro-methoxy compound **2i**). Detailed photophysical properties of selected thioxanthones will be discussed in a forthcoming paper. In addition, some other physical properties of the new photosensitizers and photoinitiators (such as melting points, solubility in solvents or polymers) can be adjusted to the desired ranges by variation of the ester function in the 1-position without substantially altering the photophysical properties. Thus 9-oxo-9*H*-thioxanthene-1-carboxylic-acid derivatives can be tailor-made photosensitizers and photoinitiators for a wide range of applications.

We thank Miss *K. Fluri* for her technical assistance.

Experimental Part

General Remarks. See [1]. Preparation of the 3-arylthio-5-nitrophthalic acids and anhydrides, see [1]. UV spectra: generally $CHCl_3$ as solv.; only the absorption with longest wavelength is given: λ_{max} in nm (ε_{max}).

*3-Nitro-9-oxo-9*H*-thioxanthene-1-carboxylic Acid* (**2b**). *Method A.* To a soln. of 5-nitro-3-(phenylthio)-phthalic anhydride (**1b**; 158.85 g, 527 mmol) in 1,1,2,2-tetrachloroethane (1.58 l), $AlCl_3$ (167.74 g, 1258 mmol) was added with stirring. The mixture was stirred at 120° for 3 h and evaporated at 90° under reduced pressure. The residue was stirred with 1.5 l of 2N HCl, the precipitate filtered off, washed well with H_2O, and dried at 140° under high vacuum. Recrystallisation from 2-PrOH gave 155.3 g (98%) of **2b**, m.p. 248° (dec.).

Method B. A mixture of 5-nitro-3-(phenylthio)phthalic acid (116.2 g, 364 mmol) and polyphosphoric acid (2440 g) was stirred at 200° for 5 h. The mixture was cooled and poured onto 6 l of ice-water. The suspension was stirred for 2 h, the precipitate separated, washed with H_2O, and dried. Recrystallisation from i-PrOH (with charcoal) gave 77.8 g (71%) of **2b**, m.p. 245° (dec.). IR (KBr): 3600–3000 (br.); 1715 (COOH); 1645 (C=O); 1535, 1348 (NO_2). Anal. calc. for $C_{14}H_7NO_5S$ (301.27): C 55.82, H 2.34, N 4.65, S 10.64; found: C 56.10, H 2.60, N 4.70, S 10.50%.

*7-Methyl-3-nitro-9-oxo-9*H*-thioxanthene-1-carboxylic Acid* (**2c**). A mixture of 3-(*p*-tolylthio)-5-nitrophthalic anhydride (**1c**; 12.7 g, 40.3 mmol), $AlCl_3$ (16.1 g, 121 mmol), and 1,1,2,2-tetrachloroethane (120 ml) was stirred at 120° for 20 min. The mixture was evaporated *in vacuo*, and the residue was stirred with 200 ml of 2N HCl. The precipitate was separated, washed with H_2O and dried at 140° under high vacuum. Recrystallisation from i-PrOH gave 11.29 g (89%) of **2c**, m.p. > 250° (dec.). UV: 420 (4000). IR (KBr): 3700–2500 (br.; OH, acid); 1730 (COOH); 1665 (C=O); 1545, 1355 (NO_2). ^{1}H-NMR ((D$_6$)DMSO): 13.5 (br. *s*, COOH); 8.80 (*d*, *J* = 2, H–C(2)); 8.10 (*m*, H–C(8)); 8.03 (*d*, *J* = 2, H–C(4)); 7.8–7.4 (*AB*, *J* = 8, H–C(5), H–C(6)); 2.60 (*s*, CH_3). Anal. calc. for $C_{15}H_9NO_5S$ (315.30): C 57.14, H 2.88, N 4.44, S 10.17; found: C 56.70, H 3.10, N 4.30, S 10.00.

*7-Methoxy-3-nitro-9-oxo-9*H*-thioxanthene-1-carboxylic Acid* (**2d**). A mixture of 3-(*p*-methoxyphenylthio)-5-nitrophthalic anhydride (**1d**; 2.4 g, 7.25 mmol), $AlCl_3$ (2.9 g, 21.75 mmol), and 1,1,2,2-tetrachloroethane (24 ml) was heated slowly with stirring to 120°. The mixture was cooled and evaporated, and the residue was stirred with 2N HCl. The precipitate was separated, washed with H_2O, dried, and recrystallized from i-PrOH to give 0.65 g (27%)

of **2d**, m.p. 268° (dec.). UV: 434 (3700). IR (KBr): 3700–2300 (br.; OH, acid); 1730 (COOH); 1665 (C=O); 1555, 1360 (NO_2). ^{1}H-NMR ((D_6)DMSO): 13.4 (br. *s*, COOH); 8.80 (*d*, *J* = 2, H–C(2)); 8.02 (*d*, *J* = 2, H–C(4)); 7.9–7.3 (*m*, H–C(5), H–C(6), H–C(8)); 3.88 (*s*, CH_3O). Anal. calc. for $C_{15}H_9NO_6S$ (331.30): C 54.38, H 2.74, N 4.23, S 9.68; found: C 54.10, H 3.00, N 4.10, S 9.80.

*7-Methyl-3-nitro-9-oxo-9*H-*xanthene-1-carboxylic Acid* (**2a**). A mixture of 5-nitro-3-(*p*-tolyloxy)phthalic anhydride (**1a**; 56.1 g, 187 mmol), $AlCl_3$ (54.9 g, 412 mmol), and 1,1,2,2-tetrachloroethane (400 ml) was stirred at 80° for 1 h. The mixture was evaporated and the residue stirred with 2N HCl. The precipitate was separated, washed with H_2O, and dissolved in THF/toluene. The soln. was dried with Na_2SO_4 and evaporated. Recrystallisation from dioxane gave 48.9 g (87%) of **2a**, m.p. 236–7°. UV: 370 (5000). IR (KBr): 3700–2000 (br., COOH); 1730 (COOH); 1680 (C=O); 1550, 1350 (NO_2). ^{1}H-NMR ((D_6)DMSO): 13.0 (br. *s*, COOH); 8.43 (*d*, *J* = 2, H–C(2)); 8.09 (*d*, *J* = 2, H–C(4)); 7.88 (*m*, H–C(8)); 7.9–7.4 (*AB*, *J* = 9, H–C(5), H–C(6); H–C(6); signal: *J'* = 2); 2.38 (*s*, CH_3). Anal. calc. for $C_{15}H_9NO_6$ (299.24): C 60.21, H 3.03, N 4.68; found: C 59.80, H 3.10, N 4.60.

*Methyl 3-Nitro-9-oxo-9*H-*thioxanthene-1-carboxylate* (**2f**). To dry CH_3OH (1.4 l), **2b** (40.3 g, 130 mmol) was added, the mixture cooled to 5–10°, treated with dry HCl for 8 h, and then refluxed for 12 h. The mixture was poured onto 3 l of H_2O. The pH was adjusted to 7–8 by addition of solid $NaHCO_3$, and the precipitate was separated and dried. Recrystallisation from toluene gave 26,6 g (65%) of **2f**, m.p. 197°. UV: 411 (4380). IR (KBr): 1750 (COOR); 1655 (C=O). Anal. calc. for $C_{15}H_9NO_5S$ (315.30): C 57.14, H 2.88, N 4.44, S 10.17; found: C 57.16, H 2.83, N 4.41, S 10.10.

*Ethyl 3-Nitro-9-oxo-9*H-*thioxanthene-1-carboxylate* (**2g**). A mixture of **2b** (70 g, 232.2 mmol), EtOH (700 ml), and conc. H_2SO_4 (14 ml) was refluxed over night, and the reaction H_2O was removed by azeotropic distillation with CCl_4. The procedure was repeated 3 times. When no more acid was present, the mixture was neutralized with $NaHCO_3$ soln. and evaporated. The residue was extracted with CH_2Cl_2 and the org. phase dried with Na_2SO_4 and evaporated. Recrystallisation from CH_3CN gave 57.65 g (75%) of **2g**, m.p. 173–5°. UV: 411 (4350). IR (CH_2Cl_2): 1720 (COOR); 1640 (C=O); 1530, 1340 (NO_2). ^{1}H-NMR ($CDCl_3$): 8.43 (*m*, H–C(8)); 8.35 (*d*, *J* = 2, H–C(2)); 8.03 (*d*, *J* = 2, H–C(4)); 7.7–7.3 (*m*, H–C(5), H–C(6), H–C(7)); 4.57 (*q*, *J* = 7, CH_2O); 1.48 (*t*, *J* = 7, CH_3). Anal. calc. for $C_{16}H_{11}NO_5S$ (329.33): C 58.36, H 3.37, N 4.26, S 9.74; found: C 57.90, H 3.60, N 4.50, S 9.90.

*Ethyl 3-Amino-9-oxo-9*H-*thioxanthene-1-carboxylate* (**4**). At 25°, **2g** (3 g, 9.12 mmol), in DMF (60 ml) were hydrogenated over 5% Pd/C (0.9 g) for 4 h. Filtration and evaporation gave 2.7 g (100%) of **4**, m.p. > 250°. UV: 332 (10 600). IR (KBr): 3450, 3340, 3250 (NH_2); 1730 (COOR); 1660 (C=O). Anal. calc. for $C_{16}H_{13}NO_3S$ (299.34): C 64.20, H 4.38, N 4.68, S 10.71; found: C 63.60, H 4.45, N 4.55, S 10.30.

*Butyl 7-Methyl-3-nitro-9-oxo-9*H-*thioxanthene-1-carboxylate* (**2h**). A mixture of **2c** (3.2 g, 10.15 mmol) and oxalyl chloride (20 ml) was refluxed for 5 h. The mixture was evaporated and the residue treated at 0° with 20 ml of BuOH. The resulting mixture was refluxed for 30 min and evaporated. Recrystallisation from toluene/cyclohexane gave 2.7 g (72%) of **2h**, m.p. 164–7°. IR (CH_2Cl_2): 1750 (COOR); 1635 (C=O); 1540, 1365 (NO_2). ^{1}H-NMR ($CDCl_3$): 8.33 (*d*, *J* = 2, H–C(2)); 8.22 (*m*, H–C(8)); 8.00 (*d*, *J* = 2, H–C(4)); 7.5–7.2 (*m*, H–C(5), H–C(6)); 4.49 (*t*, *J* = 6.5, CH_2O); 2.47 (*s*, CH_3Ar); 2.0–1.2 (*m*, CH_2CH_2); 1.04 (*t*, *J* = 6, CH_3). Anal. calc. for $C_{19}H_{17}NO_5S$ (371.41): C 61.45, H 4.62, N 3.77, S 8.63; found: C 61.15, H 4.51, N 3.96, S 8.60.

*Butyl 7-Methyl-3-nitro-9-oxo-9*H-*xanthene-1-carboxylate* (**2e**). A mixture of **2a** (2 g, 6.68 mmol) and oxalyl chloride (10 ml) was refluxed for 17 h. The mixture was evaporated and the residue refluxed with 20 ml of BuOH for 1 h. On cooling, 2.24 g (95%) of **2e** separated out, m.p. 149–50°. UV: 368 (5000). IR (CH_2Cl_2): 1750 (COOR); 1680 (C=O); 1550, 1365 (NO_2). ^{1}H-NMR ($CDCl_3$): 8.30 (*d*, *J* = 2, H–C(2)); 7.97 (*d*, *J* = 2, H–C(4)); 7.93 (*m*, H–C(8)); 7.62 (*dd*, *J* = 9, 2,1H), 7.38 (*d*, *J* = 9, 1H; H–C(5), H–C(6)); 4.47 (*t*, *J* = 6, CH_2O); 2.43 (*s*, CH_3Ar); 2.1–1.2 (*m*, CH_2CH_2); 0.98 (*t*, *J* = 6, CH_3). Anal. calc. for $C_{19}H_{17}NO_6$ (355.35): C 64.22, H 4.82, N 3.94; found: C 64.20, H 4.90, N 3.90.

N,N-*Dibutyl-7-methoxy-3-nitro-9-oxo-9*H-*thioxanthene-1-carboxamide* (**2i**). A mixture of **2d** (100 mg, 0.302 mmol), 1 drop of pyridine, $SOCl_2$ (54 mg, 0.453 mmol), and CH_2Cl_2 (1.5 ml) was stirred at 25° for 1 h. The clear soln. was evaporated, and the residue was treated with *N,N*-dibutylamine (117 mg, 0.906 mmol), in 10 ml of benzene, at 25° for 30 min. The mixture was evaporated and the residue dissolved in CH_2Cl_2/H_2O. The org. layer was separated and evaporated. Recrystallisation from CH_3OH/H_2O gave 109 mg (82%) of **2i**, m.p. 130–3°. UV: 436 (4360). ^{1}H-NMR ($CDCl_3$): 8.40 (*d*, *J* = 2, H–C(2)); 7.98 (*m*, 1H), 7.95 (*d*, *J* = 2, 1H; H–C(4), H–C(8)); 7.7–7.1 (*m*, H–C(5), H–C(6)); 3.90 (*s*, CH_3O); 3.60 (br. *t*, *J* = 7.5, 2H), 3.07 (br. *t*, *J* = 7.5, 2H; $N(CH_2–C)_2$, not equiv.); 2.2–0.5 (br. *m*, $2CH_2CH_2$); 1.06 (*t*, *J* = 6, 3H), 0.78 (*t*, *J* = 6, 3H; $2CH_3$, not equiv.). Anal. calc. for $C_{23}H_{26}N_2O_5S$ (442.53): C 62.43, H 5.92, N 6.33, S 7.25; found: C 61.90, H 5.92, N 6.00, S 7.00.

*Methyl 3-(*p*-Chlorophenylthio)-9-oxo-9*H-*thioxanthene-1-carboxylate* (**3a**). A mixture of **2f** (1 g, 3.17 mmol), *p*-chlorothiophenol (0.55 g, 3.81 mmol), anh. K_2CO_3 (1.6 g, 11.42 mmol), and DMF (10 ml) was stirred at 25° for 2 h. The mixture was evaporated *in vacuo* and the residue dissolved in CH_2Cl_2/H_2O. The org. phase was dried over

Na_2SO_4 and evaporated. Recrystallisation from toluene gave 1.11 g (85%) of **2a**, m.p. 169–70°. UV: 380 (6680). IR (CH_2Cl_2): 1740 (COOR); 1645 (C=O). ^{1}H-NMR ($CDCl_3$): 8.40 (*m*, H–C(8)); 7.6–7.2 (*m*, H–C(5), H–C(6), H–C(7), C_6H_4Cl); 7.14 (*d*, *J* = 2, 1H), 7.01 (*d*, *J* = 2, 1H; H–C(2), H–C(4)); 3.99 (*s*, $COOCH_3$). Anal. calc. for $C_{21}H_{13}ClO_3S_2$ (412.91): C 61.90, H 3.18, Cl 8.59, S 15.53; found: C 61.20, H 3.10, Cl 8.60, S 15.50.

*Ethyl 3-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecylthio)-9-oxo-9*H*-thioxanthene-1-carboxylate* (**3b**). A mixture of **2g** (3.02 g, 9.19 mmol), n-$C_8F_{17}CH_2CH_2SH$ (5.3 g, 11.02 mmol), anh. K_2CO_3 (3.8 g, 27.56 mmol), and DMF (90 ml) was stirred at 25° for 1 h. The mixture was evaporated and the residue dissolved in CH_2Cl_2/H_2O. The org. extracts were washed with H_2O, dried with Na_2SO_4, and evaporated. Recrystallisation from toluene gave 6.9 g (99%) of **3b**, m.p. 149–51°. UV: 380 (6300). IR (CH_2Cl_2): 1755 (COOR); 1665 (C=O); 1250, 1230 (very *s*, C–F). ^{1}H-NMR ($CDCl_3$): 8.43 (*m*, H–C(8)); 7.65–7.4 (*m*, H–C(5), H–C(6), H–C(7)); 7.31 (*d*, *J* = 2, 1H), 7.19 (*d*, *J* = 2, 1H; H–C(2), H–C(4)); 4.55 (*q*, *J* = 7, CH_2O); 3.33 (*t*, *J* = 7, CH_2S); 3.0–2.1 (br. *m*, CH_2CF_2); 1.50 (*t*, *J* = 7, CH_3). Anal. calc. for $C_{26}H_{15}F_{17}O_3S_2$ (762.49): C 40.96, H 1.98, F 43.26, S 8.41; found: C 40.90, H 1.80, F 42.50, S 8.50.

*Ethyl 3-Methylsulfonyl-9-oxo-9*H*-thioxanthene-1-carboxylate* (**3c**). A mixture of **2g** (2 g, 6.08 mmol), sodium methanesulfinate (1.245 g, 12.2 mmol), and DMF (15 ml) was stirred at 80° for 3 h. The mixture was evaporated and the residue dissolved in CH_2Cl_2/H_2O. The org. extract was washed with H_2O, dried over Na_2SO_4 and evaporated. Recrystallisation from toluene gave 1.9 g (86%) of **3c**, m.p. 184–6°. UV: 399 (5970). ^{1}H-NMR ($CDCl_3$): 8.48 (*m*, H–C(8)); 8.19 (*d*, *J* = 2, H–C(2)); 7.87 (*d*, *J* = 2, H–C(4)); 7.7–7.3 (*m*, H–C(5), H–C(6), H–C(7)); 4.51 (*q*, *J* = 7, CH_2O); 3.14 (*s*, CH_3SO_2); 1.44 (*t*, *J* = 7, CH_3CH_2O). Anal. calc. for $C_{17}H_{14}O_5S_2$ (362.41): C 56.34, H 3.90, S 17.69; found: C 56.60, H 3.90, S 17.80.

*Ethyl 3-Phenylsulfonyl-9-oxo-9*H*-thioxanthene-1-carboxylate* (**3d**). A mixture of **2g** (10.0 g, 30.36 mmol), sodium benzenesulfinate (9.97 g, 60.73 mmol), and DMF (50 ml) was stirred at 120° for 2 h. The mixture was evaporated *in vacuo* and the residue dissolved in CH_2Cl_2/H_2O. The org. phase was separated, washed with H_2O, dried with Na_2SO_4 and evaporated. Recrystallisation from toluene gave 10.81 g (79%) of **3d**, m.p. 211–3°. UV: 401 (5760). IR (CH_2Cl_2): 1730 (COOR); 1645 (C=O); 1320, 1270, 1170, 1140 (Ar-SO_2-Ar'). ^{1}H-NMR ($CDCl_3$): 8.38 (*m*, H–C(8)); 8.12 (*d*, *J* = 2, H–C(2)); 7.93 (*m*, 2H), 7.65–7.1 (br. *m*, 6H; $C_6H_5SO_2$, H–C(5), H–C(6), H–C(7)); 7.77 (*d*, *J* = 2, H–C(4)); 4.48 (*q*, *J* = 7, CH_2O); 1.41 (*t*, *J* = 7, CH_3). Anal. calc. for $C_{22}H_{16}O_5S_2$ (424.49): C 62.25, H 3.80, S 15.11; found: C 62.40, H 4.00, S 14.90.

*Methyl 3-Methoxy-9-oxo-9*H*-thioxanthene-1-carboxylate* (**3e**). A mixture of **2f** (2 g, 6.35 mmol), 1.0M $NaOCH_3$ in CH_3OH (9.53 ml, 9.53 mmol) and further 10 ml of dry CH_3OH was refluxed for 1 h. The mixture was diluted with toluene and evaporated *in vacuo*. The residue was dissolved in CH_2Cl_2/H_2O and the org. extract dried and evaporated. Recrystallisation from CH_2Cl_2/pentane gave 1.64 g (86%) of **3e**, m.p. 163–5°. UV: 368 (3000). ^{1}H-NMR ($CDCl_3$): 8.48 (*m*, H–C(8)); 7.8–7.2 (br. *m*, H–C(5), H–C(6), H–C(7)); 6.94 (*m*, H–C(2), H–C(4)); 4.03 (*s*, $COOCH_3$); 3.84 (*s*, CH_3O). Anal. calc. for $C_{15}H_{12}O_4S$ (288.32): C 62.49, H 4.20, S 11.12; found: C 62.75, H 4.07, S 11.01.

*Ethyl 3-Azido-9-oxo-9*H*-thioxanthene-1-carboxylate* (**3f**). A mixture of **2g** (3 g, 9.1 mmol), NaN_3 (0.9 g, 13.7 mmol), and DMF (20 ml) was stirred at 80° for 1 h. The mixture was evaporated *in vacuo* at 50°, and the residue was extracted with CH_2Cl_2. The extracts were dried over Na_2SO_4 and evaporated below 50° to give 2.96 g (100%) of **3f**, m.p. 154–6°. UV: 361 (6060). IR (CH_2Cl_2): 2120 (N_3); 1730 (COOR); 1640 (C=O). ^{1}H-NMR ($CDCl_3$): 8.43 (*m*, H–C(8)); 7.6–7.2 (br. *m*, H–C(5), H–C(6), H–C(7)); 7.00 (*d*, *J* = 2, 1H), 6.87 (*d*, *J* = 2, 1H; H–C(2), H–C(4)); 4.46 (*q*, *J* = 7, CH_2O); 1.38 (*t*, *J* = 7, CH_3). Anal. calc. for $C_{16}H_{11}N_3O_3S$ (325.34): C 59.07, H 3.41, N 12.92; found: C 59.08, H 3.53, N 12.84.

*3-Chloro-9-oxo-9*H*-thioxanthene-1-carboxylic Acid* (**3h**). A mixture of **2b** (3 g, 9.96 mmol) and $SOCl_2$ (20 ml) was refluxed for 48 h and then evaporated. The residue was refluxed with H_2O for 30 min. After cooling, the precipitate was filtered off, washed with H_2O and dissolved in THF/toluene. The soln. was dried with Na_2SO_4 and evaporated to give 2.65 g (92%) of **3h**, m.p. 268–71°. UV: 382 (5800). ^{1}H-NMR ((D_6)DMSO): 13.1 (br. *m*, COOH); 8.38 (*m*, H–C(8)); 8.09 (*d*, *J* = 2, H–C(2)); 7.9–7.5 (br. *m*, H–C(5), H–C(6), H–C(7)); 7.55 (*d*, *J* = 7, H–C(4)). Anal. calc. for $C_{14}H_7ClO_3S$ (290.72): C 57.84, H 2.43, Cl 12.20, S 11.03; found: C 57.50, H 2.60, Cl 11.50, S 10.80.

*Ethyl 3-Chloro-9-oxo-9*H*-thioxanthene-1-carboxylate* (**3i**). A mixture of **2b** (1 g, 3.32 mmol) and $SOCl_2$ (10 ml) was refluxed for 48 h and then evaporated. The residue was refluxed with 10 ml of abs. EtOH for 1 h, and the mixture was evaporated. Recrystallisation from EtOH/CH_3CN gave 0.82 g (77%) of **3i**, m.p. 133–5°. UV: 382 (6440). IR (CH_2Cl_2): 1730 (COOR); 1645 (C=O). ^{1}H-NMR ($CDCl_3$): 8.44 (*m*, H–C(8)); 7.6–7.2 (br. *m*, 5 arom. H); 4.47 (*q*, *J* = 7, CH_2O); 1.40 (*t*, *J* = 7, CH_3). Anal. calc. for $C_{16}H_{11}ClO_3S$ (318.77): C 60.29, H 3.48, Cl 11.12, S 10.06; found: C 60.20, H 3.40, Cl 11.20, S 10.00.

*Butyl 3-Bromo-9-oxo-9*H*-thioxanthene-1-carboxylate* (**3l**). A mixture of **2b** (602 mg, 2 mmol) and PBr_3 (17 g, 62.8 mmol) was stirred at 110° for 18 h. Under cooling 20 ml of BuOH were added dropwise, and the mixture was

refluxed for 30 min and evaporated. The residue was stirred with aq. $NaHCO_3$ soln. and extracted into CH_2Cl_2. The extracts were washed with brine, dried over Na_2SO_4, and evaporated. The residue was chromatographed with CH_2Cl_2 on silica gel to give 160 mg (20%) of **31**, m.p. 117–20°. UV: 383 (6000). IR (CH_2Cl_2): 1755 (COOR); 1670 (C=O). ^{1}H-NMR ($CDCl_3$): 8.45 (*m*, H–C(8)); 7.71 (*d*, J = 2, H–C(2)); 7.65–7.4 (br. *m*, 4 arom. H); 4.43 (*t*, J = 6.5, CH_2O); 2.1–0.8 (br. *m*, $CH_3CH_2CH_2$). Anal. calc. for $C_{18}H_{15}BrO_3S$ (391.28): C 55.26, H 3.87, Br 20.42; found: C 54.72, H 3.78, Br 19.17.

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