Photochromic heteroaromatic thiofulgides and dimethoxybutanoic acid lactones

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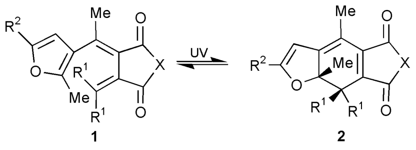
Thiofulgides 1, (X = S) cyclise on irradiation with UV light to form thermally stable photochromes 2, (X = S) that absorb at much longer wavelengths than photochromes 2, (X = O), formed from corresponding fulgides 1, (X = O), reverse reactions occur on exposure to white light; photochromic thiofulgides are prepared by reaction of fulgides with sodium hydrosulfide in hot toluene and photochromic lactones 9 and 12 are prepared by reaction of fulgides with sodium hydrosulfide in cold methanol followed by cyclisation with a carbodiimide.

Photochromic heteroaromatic thiofulgides **1**, (X = S) are of special interest because their coloured forms **2**, (X = S) have the potential to show large bathochromic shifts of their long wavelength absorption bands compared to the coloured forms **2**, (X = O) from corresponding fulgides **1**, (X = O). (The effect of replacement of oxygen by sulfur can be seen in the ultraviolet spectra of thiomaleic anhydride[2] which shows λ_{max} 230 nm compared to λ_{max} 198 nm for maleic anhydride[3].)



Previous attempts to synthesise photochromic heteroaromatic thiofulgides by methods used for the preparation of acetic,[4] succinic,[5] phthalic,[6] and dibenzylidenesuccinic thioanhydrides[7] were unsuccessful.

We find that (*Z*)-thiofulgides, (*Z*)-4-dicyclopropylmethylene[1-(2,5-dimethyl-3-furyl) and (2-methyl-5-phenyl-3-furyl)-ethylidene]thiosuccinic anhydrides **6a** and **6b** can be prepared

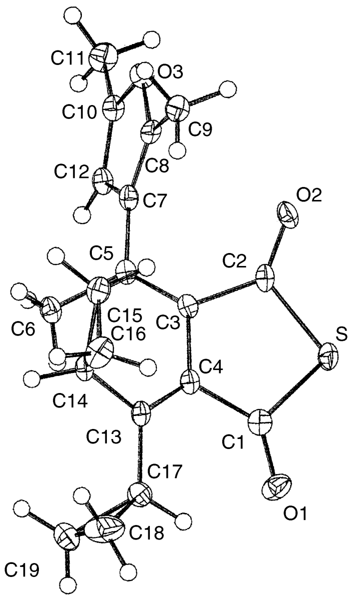


Fig. 1 The X-ray structure of (*Z*)-thiofulgide **6a**.

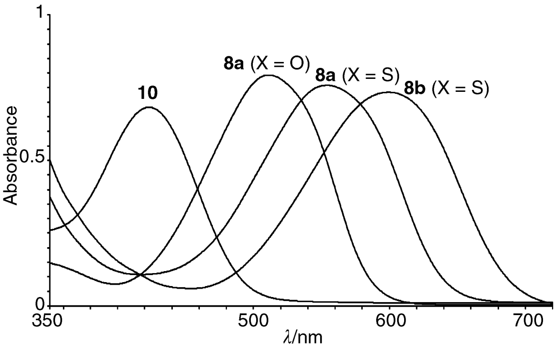
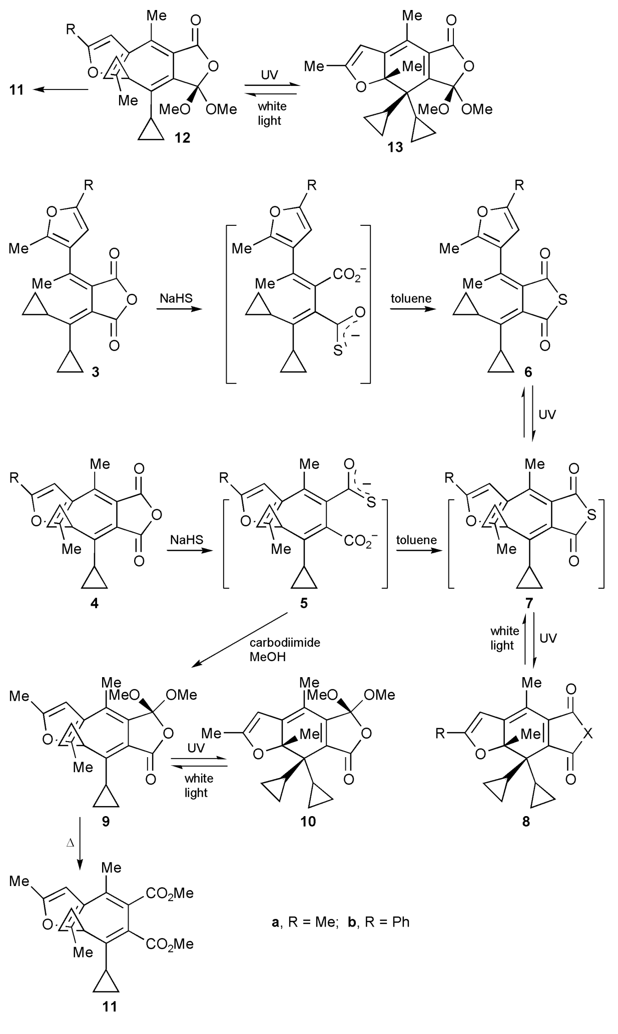


Fig. 2 The spectra of compounds **10**, **8a** (X = O), **8a** (X = S), and **8b** (X = S) (λ_{max} 424, 511, 544, and 599 nm respectively) obtained after irradiation at 366 nm of compounds **9**, **4a**, **6a** (X = S) and **6b** (X = S) (1×10^{-4} molar solutions in toluene) to the photostationary state, illustrating the major colour changes which can be achieved by molecular tailoring.



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by boiling (4 h) (*Z*)-fulgides **3a** and **3b** (1 g) in toluene with 2–3 eq. of yellow sodium hydrosulfide (Aldrich). They were obtained as yellow crystals, mp 133 and 147–8 °C respectively, after purification by column chromatography and crystallisation from dichloromethane and petroleum. Seven photochromic thiofulgides have been prepared in yields of *ca.* 35% by this general method. Yields depend on the quality of sodium hydrosulfide, which deteriorates with time.

The structure and stereochemistry of (*Z*)-thiofulgide **6a** was established by X-ray crystallographic analysis† (Fig. 1).

On irradiation (366 nm), (*Z*)-thiofulgides **6a** and **6b** in toluene isomerised to (*E*)-thiofulgides **7a** and **7b** which cyclised to thermally stable purple and blue photochromes **8a** (X = S) and **8b** (X = S), showing bathochromic shifts (40 and 60 nm) of the maxima of their long wavelength absorption bands compared to the red and magenta photochromes **8a** (X = O) and **8b** (X = O) (Fig. 2). On exposure to white light, photochromes **8a** (X = S) and **8b** (X = S) ring opened to pale yellow (*E*)-thiofulgides **7a** and **7b**. Quantum efficiencies for colouring (Øc) at 366 nm for (*E*)-thiofulgides in toluene were less than for corresponding (*E*)-fulgides. Øc for thiofulgide **1** ($R^1 = R^2 =$ Me, X = S) was 9% compared to 20% for fulgide **1** ($R^1 = R^2 =$ Me, X = O). Preliminary studies indicate that bleaching efficiencies and photochemical fatigue of the photochromes of thiofulgides were comparable to those of photochromes of the corresponding fulgides.

When (*E*)-fulgide **4a** was stirred with sodium hydrosulfide in MeOH at room temperature, the salt of thioacid **5** was formed which after treatment with 1-ethyl-3-(dimethylamino)propylcarbodiimide HCl, reacted with methanol to give **9** (colourless crystals, mp 168–9 °C, 33% yield). On irradiation (366 nm), lactone **9** in toluene cyclised to the thermally stable bright intensely coloured yellow photochrome **10** which underwent the reverse reaction on exposure to white light.

(*Z*)-Fulgide **3** gave the colourless lactone **12** in 31% yield in an analogous reaction which cyclised to the pale yellow photochrome **13** on irradiation at 366 nm.

Lactones **9** and **12** were converted quantitatively into **11** on boiling with sodium hydrosulfide in MeOH, exemplifying a convenient method of preparing dimethyl esters from anhydrides. All new compounds were fully characterised.

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Notes and references

† *Crystal data for* **6a**: $C_{19}H_{20}O_3S$, M = 328.4, monoclinic, space group $P2(1)/n$, a = 10.773(2), b = 7.861(2), c = 19.492(4) Å, β = 92.42(3)°, V = 1649.2(6) Å^3, T = 150(2) K, Z = 4, D_c = 1.323 g cm^3, R_1 = 0.0686, wR_2 = 0.1179 for all 2349 data and 211 parameters. Data were recorded using a FAST TV area detector diffractometer and Mo-Kα radiation. CCDC 182/1709. See http://www.rsc.org/suppdata/cc/b0/b002033h/ for crystallographic files in .cif format.

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