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Photochromic Fulgides: Part 2. Synthesis and Photochromic Properties of 1-[2,5-Dimethyl-3-furyl or 3-thienyl) ethylidene] diphenylmethylene Succinic Anhydrides and [di(4-fluoro-phenyl) methylene]-1-[2,5-dimethyl-3-furyl) ethylidene] Succinic Anhydride

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ABSTRACT. Two novel fulgides were prepared and their photochromic properties were studied. The orange fulgides **3a-c** undergoes a reversible photochemical reactions to give the deep red **5a-c** which is thermally stable at room temperature. Changing the heteroatom from oxygen to sulphur causes a 40nm bathochromic shift of the long maxima wavelength.

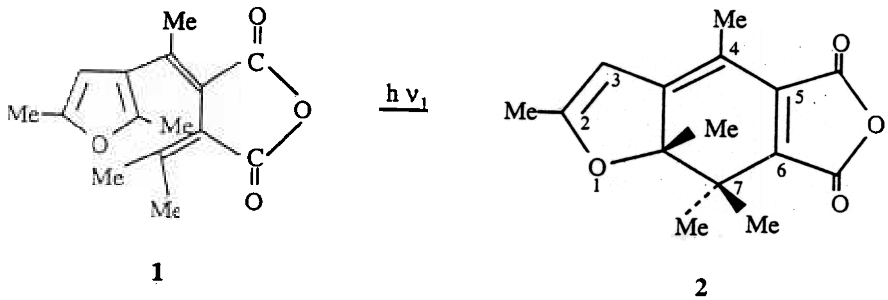
Introduction

Darcy *et al.*[1], reported the first photochromic fatigue free fulgide **1** and demonstrated the high efficiency for colouring to give 7, 7a-dihydrobenzofuran (7,7a-DHBF) **2,** when irradiated at 366nm (Scheme 1).

The thermal stability of **2** is due to the presence of the 7a-methyl group. Compound (1) is used as an actinometer in the range 310-370nm and 435-545nm[2].

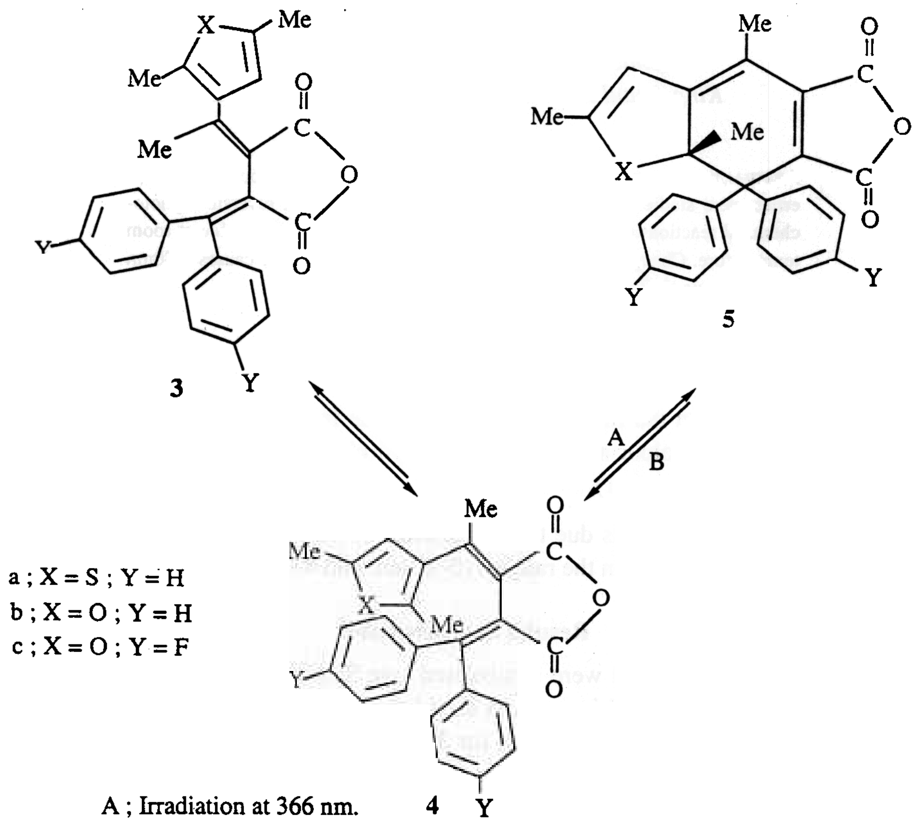
Results and Discussion

The three compounds used were synthesised via Stobbe condensation. Compounds **3a** and **3c** were obtained as Z-isomers as established from their ^{1}H-nmr spectra which showed a high field singlets at 1.43ppm for **3a** and at 1.50ppm for **3c** attributed to the ethylidene methyl. On the other hand, compound **4b** was obtained as E-isomer as established from the ethylidene methyl singlet at 2.43ppm deshielded by the adjacent carbonyl group.



Scheme 1

Z-1-[2,5-dimethyl-3-thienyl) ethylidene] diphenylmethylenesuccinic anhydride **3a** in toluene undergoes ring closure process on irradiation at 366nm to give the thermally stable 7,7-diphenyl -2,4, 7a-trimethyl-dihydrobenzofuran 55-6-dicarboxylic anhydride (7,7a-DHBF) **5a,** which was stable at room temperature. On exposure to white light, the 7,7a-DHBF reverts back to the original fulgide **3a** (Scheme 2).



A ; Irradiation at 366 nm.

B; Irradiation at 546 nm.

Scheme 2

Substitution of sulphur atom in the heterocyclic ring by oxygen causes a remarkable hypsochromic shift. It was of interest to see the effect of introduction of substituents on the phenyl rings, compound **3c** was prepared and investigated and found to have similar photochemical behaviour.

Table 1 summarises the UV-Visible data of the open and closed forms of fulgides, **3a, 3c** and **3b.**

Table 1. Spectroscopic data of fulgides **3a, 3c** and **4b** and their 7,7a-DHBF **5a-c.**

Compounds	Uncoloured forms		Coloured forms	
	λ max/nm	ε*	λ max/nm	ε*
3a	388	9400	536	2600
3c	405	5580	490	-
4b	406	7070	488	4380

*$dm^3\ mol^{-1}\ cm^{-1}$ (for 10^{-4} M solution in toluene)

Conclusion

The effects of changing the heteroatom from oxygen to sulphur causes a marked bathochromic shift of the long wavelength of the cyclised forms. On the other hand substituents on both phenyl groups causes no change in the position of the maxima absorption of 7,7a-DHBFS.

Experimental

Melting points were determined on a Reichardt hot-stage apparatus and were uncorrected. UV and Visible spectra were measured for a 10^{-4} M solutions in toluene. NMR spectra were obtained for solutions in deuteriochloroform with TMS as internal standard using a Bruker WM 360 spectrometer. Mass spectra were recorded on a varian Mat. CH5 spectrometer. Infrared spectra were recorded for chloroform solution. Solvents were dried prior to use.

The solutions were irradiated at 366nm, using a 100W mercury discharge lamp with a filter (type OX1, chance pilkington)..

General Procedure for Stobbe Condensation

Diethyl diphenylmethylenesuccinate

A mixture of benzophenone (70g, 0.38 moles) and dimethyl succinate (50g, 0.34 moles) in toluene (150ml) was added dropwise with stirring to a suspension of potassium t-butoxide (50g, 0.45 moles) in toluene (200ml) and left to stir overnight at room temperature. Water (100ml) was added and the aqueous layer was separated, acidified and extracted into diethyl ether. After removal of the solvent the half-ester was obtained as a brown oil (68g). Esterification using acetyl chloride and methanol gave the diester as a viscous light yellow oil which solidified on standard to give yellow crystals (79.69g, 75% overall yield), m.p. 78-80°C. ^{1}H-NMR: δ 3.46 (2H, s, CH_2 protons, 3.47 (3H, s, CH_3O), 3.70 (3H, s, CH_3O), 7.10-7.36 (10H, m, aromatic protons).

Dimethyl (E)-1-[(2,5-dimethyl-3-furyl) ethylidene]-succinate

This was prepared by similar procedure as used for dimethyl diphenylmethylnesuccinate by condensing 3-acetyl-2,5-dimethylfuran (47g, 0.34 moles) and dimethyl succinate (80g, 0.55 moles). Yellow oil (41g, 45% overall yield) b.p. 150-180°C / 0.4mm Hg. ^{1}H-nmr: δ 2.10 (3H, s, CH_3) 2.24 (3H, s, CH_3), 2.30 (3H s, CH_3), 3.34 (3H, S, CH_2 protons), 3.66 (3H, s, CH_3O), 3.75 (3H, s, CH_3O), 5.79 (1H, s, 4-furyl protons).

Dimethyl (Z)-1-[2,5-dimethyl-3-thienyl) ethylidene] -succinate

This was prepared using similar procedure described for dimethyl diphenylmethylnessuccinate by condensing 3-acetyl-2,5-dimethylthiophene (37g, 0.24 moles) and dimethyl succinate (35g, 0.24 moles). A yellow oil (43g, 64%) b.p. 140-150°C / 0.1mm Hg. ^{1}H-nmr: δ 2.21 (3H, s, CH_3), 2.32 (3H, s, CH_3), 2.40 (3H, s, CH_3), 3.23 (2H, s, CH_2 protons), 3.64 (3H, s, CH_3O), 3.78 (3H, s, CH_3O), 6.38 (1H, S, 4-thienyl protons).

Preparation of Fulgides

General Procedure

(Z)-1-[(2,5-dimethyl-3-thienyl) ethylidene] diphenylmethylene-succinic anhydride (**3a**)

A mixture of Z-dimethyl-1-[2,5-dimethyl-3-thienyl) ethylidene] succinate (15g, 0.064 moles) and benzophenone (11.6g, 0.064 moles) in toluene (50ml) was added dropwise with stirring to a suspension of potassium t-butoxide (10g, 0.09 moles) in toluene (100ml) and stirred for 12 hours. Work up as described for the first Stobbe condensation. The resulting half-easter was hydolysed by boiling with alc. KOH, followed by acidification to give the diacid which was cyclised using acetyl chloride to give compound **3a** as an orange crystals (2.6g 10% overall yield), m.p. 196-198°C (from methanol).

(Found: C, 75.17; H, 5.14%. Calc for $C_{25}H_{20}O_3S$ C75.01; H, 5.0%), m/z, 400 (100%), ^{1}H-nmr: δ 1.43 (3H, s, CH_3 trans to C = O), 2.37 (3H, s, CH_3), 2.39 (3H, s, CH_3), 6.41 (1H, s, 4-thienyl proton Z- isomer), 7.10-7.50 (10H, m, aromatic protons).

(E)-1-](2,5-dimethyl-3-furyl) ethylidene] diphenylmethylene-succinic anhydridge (**4b**)

This was prepared as described for **3a** using 3-acetyl-2,5-dimethylfuran (13.35g, 0.1 moles) and dimethyl diphenylmethylene succinate (30g, 0.1 moles). Compound **2b** & **4b** was obtained as an orange crystals (1.5g, 4%) b.p. overall yield m.p. 178-180°C (from petroleum ether) [lit.[2] 188-190°C], ^{1}H-nmr: δ 1.95 (3H, s, CH_3), 1.99 (3H, s, CH_3), 2.43 (3H, s, CH_3 cis to carbonyl group), 5.32 (1H, s, 4-furyl proton), 7.10-7.44 (10H, m, aromatic protons).

(Z)-[Di(4-fluorophenyl) methylene]-1-[(2,5-dimethyl-3-furyl) ethylidene] diphenylmethylene] succinic anhydride (**3c**)

This was prepared as described for **3a** using 4,4`-difluorobenzophenone (15g, 0.07 moles) and dimethyl (E)-2-5-dimethyl-3-furylethylidene succinate (14g, 0.053 moles). Compound **3c** was obtained as an orange crystals (1.5g, 6.7% overall yield), m.p. 199-202°C (from methanol).

(Found: C, 71.30; H, 4.36%. Calc for $C_{25}H_{18}O_4F_2$ C, 71.44; H, 2.28%), m/z, 420; ^{1}H-nmr: δ 1.5 (3H, s, CH_3), 2.22 (3H, s, CH_3), 2.3 (3H, s, CH_3 cis to carbonyl group), 5.88 (1H, s, 4-furyl proton) 7.0-7.30 (8H, m, aromatic protons) ν_{max}/cm^{-1} 1810 (C = O), 1763 (C = O).

References

[1] **Darcy, P.J., Heller, H.G., Strydom, P.J.** and **Whittall, J.**, *J. Chem. Soc. Perkin Trans*, 1981, **I**, 202.
[2] **Darcy, P.J.**, *Studies on Fatigue-Resistant Photochromic Fulgides*, Ph.D. Thesis, University of Wales, College of Aberystwyth, 1977.

مركبات الفلجـايد ذات التغير اللـوني بفعـل الضـوء الجـزء الثـاني : تحضـير ودراسـة لخـواص اللونيـة لمـركبات ١-[٢ , ٥-ثنائي ميثيل-٣-فيورايل أو ٣-ثينايل) ايثيلدين ثنائي فينيل الميثيلين) أنهيدريدات حامض السكسينك] و [ثنائي (٤-فلوروفينيل) ميثلين]-١-[٢ , ٥ ثنائي ميثيل-٣-فيورايل) ايثيلدين] أنهيدريدات حامض السكسينك

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المستخلص . تم تحضير مركبين جديدين ينتميان إلى سلسلة الفلجايدات وتم دراسة خواصهما اللونية الضوئية قبل وبعد عملية التشعيع . المركب البرتقالي 3 a-c تحول في عملية عكسية ضوئية إلى اللون الأحمر الداكن 5 a-c الثابت عند درجة حرارة معتدلة . تغير الذرة في الحلقة غير المتجانسة من أوكسجين إلى كبريت سبب إزاحة في طول موجة قمة الامتصاص للشكل الملون 5 a-c .