

# Photochromic Fulgides: Part 1. Synthesis and Photochromic Properties of Di(4-chlorophenyl), Di(4-fluorophenyl) isopropylidene Succinic Anhydrides and E,Z-(isopropylidene- 4-methylphenyl) phenylmethylene Succinic Anhydride

ABDULLAH M. ASIRI

*Chemistry Department, Faculty of Science,  
King Abdulaziz University, Jeddah, Saudi Arabia*

**ABSTRACT.** Three novel fulgides were synthesised and their photochromic properties were studied. Substituent in the position 4 of one or both phenyl groups has remarkable effect on the absorption maxima of both the coloured and the uncoloured forms.

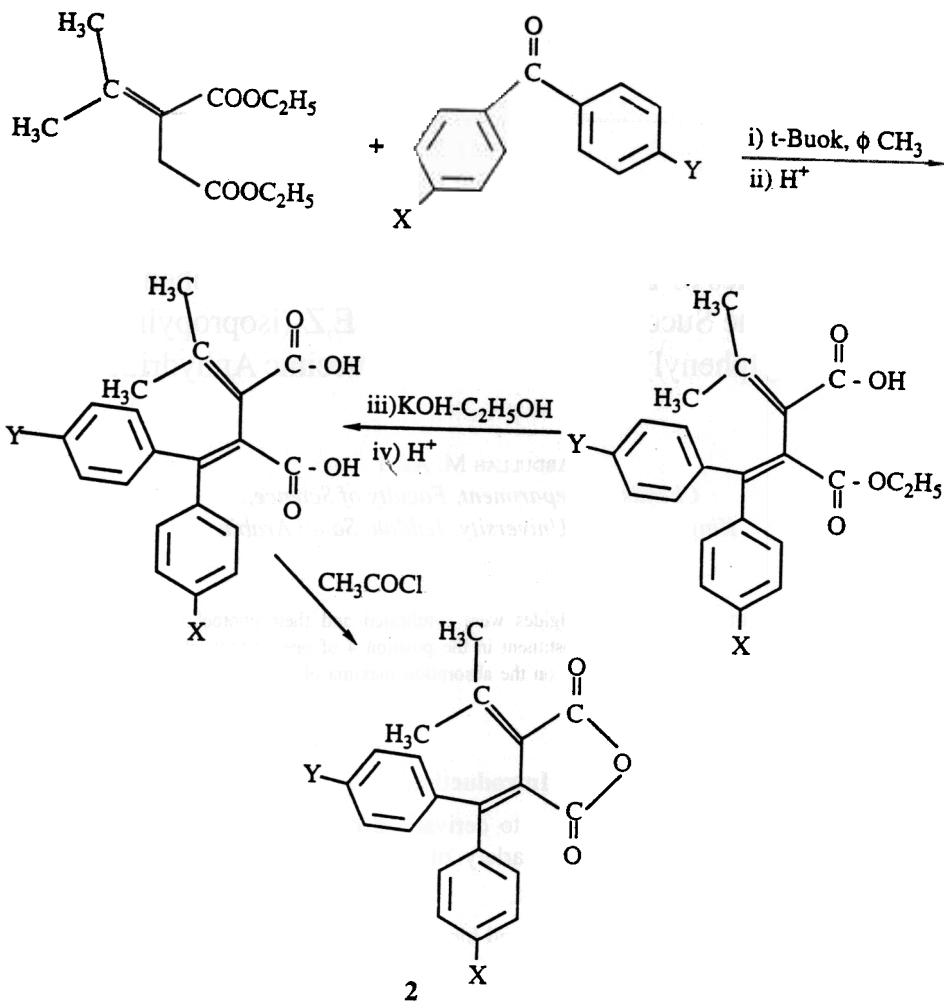
## Introduction

Stobbe introduced the term "Fulgide" to derivatives of 3,4-bis-substituted methylene succinic anhydride and described a variety of their thermal and photochemical reactions<sup>[1]</sup>.

The photochromism of phenyl substituted bis-methylene succinic anhydride "Fulgides" in the solid state was first discovered by Stobbe<sup>[1]</sup>, while the photochromic mechanism of phenyl-substituted fulgides was first postulated by Becker and Santiago<sup>[2]</sup> and confirmed later by Hart *et al.*<sup>[3]</sup> and Hart and Heller<sup>[4]</sup>. They demonstrated that the photochromic reaction is an electrocyclic reaction, *i.e.* the coloured form arises by a conrotatory ring closure of fulgide in accordance with the Woodward-Hoffman selection rules<sup>[5]</sup>.

## Results and Discussion

In this paper, three fulgides **2a-c** were prepared via Stobbe condensation using potassium t-butoxide as a base in toluene as shown in Scheme 1. Fulgides **2d-e** were obtained as a 1:1 mixture of E(d) and Z(e) isomers as established from their <sup>1</sup>H-nmr spectrum. Table 1 summarises the <sup>1</sup>H-nmr data of compounds **2a-e**. Irradiation of compounds **2a-c** and a 1:1 mixture of E and Z isomers **2d** and **2e** in both solid and solution with ultraviolet light gave a yellow to red colour.



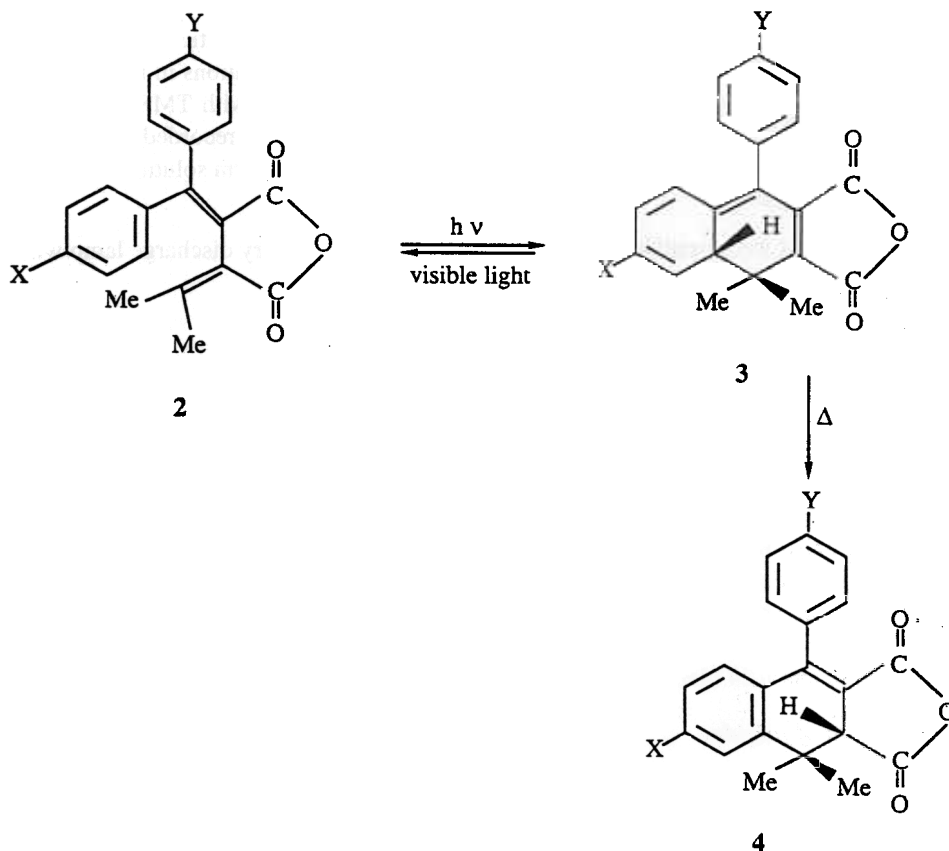
- a;  $\text{X} = \text{Y} = \text{H}$
- b;  $\text{X} = \text{Y} = \text{F}$
- c;  $\text{X} = \text{Y} = \text{Cl}$
- d;  $\text{X} = \text{H}, \text{Y} = \text{CH}_3$
- e;  $\text{X} = \text{CH}_3, \text{Y} = \text{H}$

Scheme

TABLE I. <sup>1</sup>H-NMR data for fulgides 2a-e in ppm.

Fulgide	CH <sub>3</sub> trans to C = O	CH <sub>3</sub> cis to C = O	4-CH <sub>3</sub>	Aromatic protons
2a	1.27	2.30	-	7.17 - 7.50
2b	1.31	2.31	-	7.04 - 7.26
2c	1.32	2.31	-	7.10 - 7.36
2d	1.24	2.28	2.37	7.04 - 7.46
2e	1.29	2.30	2.41	7.13 - 7.36

The red colour was attributed to the formation of (1,8a - DHNs)\* 3a-e (Scheme 2). The coloured forms revert back to the originals when exposed to white light. On prolonged irradiation, the 1,8a - DHNs underwent thermal 1,5-H - shift to give 1,2-DHNs 4a-e.



Scheme 2

\*1,8a-Dihydronaphthalene derivatives.

The introduction of halogene atom or methyl group in position 4 of the phenyl at which the cyclisation takes place causes a hypsochromic shift of the long wavelength absorption band of the 1,8a-DHN **3a-c** and a bathochromic shift of the long wavelength absorption band of the fulgides **2a-e**. The UV - Visible data of fulgides **2a-e** and their 1,8a-DHNs **3a-e** are summarised in Table 2.

TABLE 2. Spectroscopic data of fulgides **2a-e** and their 1,8a-DHNs **3a-e**.

Fulgide	$\lambda$ max/nm	$\epsilon^a$	1,8a - DHNs	$\lambda$ max/nm	$\epsilon^a$
<b>2a</b>	381	4500	<b>3a</b>	493	220
<b>2b</b>	397	2649	<b>3b</b>	483	170
<b>2c</b>	398	2905	<b>3c</b>	477	110
<b>2d/e</b>	400	2884	<b>3d/e</b>	497	180

<sup>a</sup> dm<sup>3</sup> mole<sup>-1</sup> cm<sup>-1</sup>

### Experimental

Melting points were determined on a Reichardt hot-stage apparatus and were uncorrected. UV and visible spectra were measured for a 10<sup>-4</sup> M solutions in toluene. <sup>1</sup>H-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 in chloroform solution. Solvents were dried prior to use.

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

#### *Diethyl isopropylidenesuccinate (1)*

A mixture of diethyl succinate (174g, 1 mol) and acetone (71g, 1.2 moles) in toluene (100ml) was added dropwise to a suspension of potassium t-butoxide (112g, 1 mol) in toluene (400ml) over 1 hour period at room temperature. The solution was stirred further for 12 hours, water (100ml) was added and the aqueous layer was separated and acidified using 6 M HCl. The liberated half-ester was extracted using ether (2 × 100ml) dried over anhydrous MgSO<sub>4</sub>. Solvent was distilled off leaving the crude succinic half-ester as agum. Esterification with thionyl chloride and ethanol gave the diester (93 g, 43%) as a pale yellow oil b.p. 110-115°C / 0.1 mm Hg <sup>1</sup>H nmr:  $\delta$  1.25 and 1.28 (6H, two t, 2 × CH<sub>3</sub>), 1.86 (3H, s, CH<sub>3</sub>), 2.18 (3H, s, CH<sub>3</sub> cis to C = O), 3.41 (2H, s, CH<sub>2</sub> proton, 4.20 and 4.24 (4H, two overlapped quartet, 2 × CH<sub>2</sub> protons).

#### *Preparation of fulgides*

##### *General procedure*

*Diphenylmethylene (isopropylidene) succinic anhydride (2a)*: A mixture of diethyl isopropylidenesuccinate (30g, 0.14 moles) and benzophenone (26g, 0.14 moles) in toluene (90ml) was added dropwise to a suspension of potassium t-butoxide in toluene (110ml) and stirred for 5 hours. Work up as described for **1** gave the half-ester which

was hydrolysed by boiling with alc. KOH for 6 hours to give the dipotassium salt which was acidified using 6 M HCl and the liberated diacid was extracted with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 50\text{ml}$ ). The solvent was concentrated to half and acetyl chloride (30ml) was added slowly at room temperature and stirred for 6 hours before acetyl chloride was removed under reduced pressure leaving a crude fulgide **2a** which was recrystallised from ethanol to give yellow crystals, m.p. 167-168°C (lit<sup>[4]</sup> 171.5°C).

*[Di(4-fluorophenyl) methylene] isopropylidenesuccinic anhydride (3b)*: A mixture of diethyl isopropylidenesuccinate **1** (25g, 0.12 moles) and 4,4'-difluorobenzophenone (26g, 0.12 moles) in toluene (150ml) were added to a suspension of potassium t-butoxide (14g, 0.12 moles) in toluene (150ml) work up as described for **2a** followed by hydrolysis and cyclization gave compound **2b** as yellow needles (4g, 10%), m.p. 294-196°C (from ethanol). (Found: C, 70.79; H, 4.25% calc for  $\text{C}_{20}\text{H}_{14}\text{O}_3\text{F}_2$  C, 70.58; H, 4.14%), m/z, 340,  $\nu_{\text{max}} / \text{cm}^{-1}$  1812 (C = O), 1764 (C = O).

*[Di(4-chlorophenyl) methylene] isopropylidenesuccinic anhydride (2c)*: A mixture of diethyl isopropylidenesuccinate **1** (8.5 g, 0.04 moles) and 4,4'-dichlorobenzophenone (10g, 0.04 moles) in toluene (20ml) were added to a suspension of potassium t-butoxide (4.5g, 0.04 moles) in toluene (100 ml) and stirred for 16 hours. After work up as described for **2a** followed by hydrolysis and cyclization gave compound **2c** as a pale yellow needles (2.6g, 17%), m.p. 233-235°C (from diethyl ether). (Found: C, 64.19; H, 3.59% calc for  $\text{C}_{20}\text{H}_{14}\text{O}_3\text{Cl}_2$  C, 64.34; H, 3.75%); m/z, 342(100), 374(66),  $\nu_{\text{max}} / \text{cm}^{-1}$  1815 (C = O), 1764 (C = O).

*EZ- Isopropylidene [4-methylphenyl (phenyl) methylenesuccinic anhydride (2e and 2d)*: A mixture of diethyl isopropylidenesuccinate (25g, 0.12 moles) and 4-methylbenzophenone (24g, 0.12 moles) in toluene (30ml) were added to a suspension of potassium t-butoxide (15g, 0.13 moles) in toluene (100ml) stirred for 12 hours. Work up gave the half-ester which was hydrolysed and cyclised to give a 1:1 mixture of compounds **2d** and **2e** as yellow crystals m.p. 155-160°C (from ether-petrol mixture). (Found: C, 79.44; H, 5.70% calc for  $\text{C}_{21}\text{H}_{18}\text{O}_3$  C, 79.22; H, 5.70%); m/z, 318,  $\nu_{\text{max}} / \text{cm}^{-1}$  1811 (C = O), 1761 (C = O).

### Photoreactions

A solution in toluene ca. ( $10^{-4}$  M) in a 1 cm cuvet is irradiated for 3hr at 366nm using low pressure mercury lamp of type OXI, filter which transmits only the light of 366nm.

### References

- [1] Stobbe, H., *Ber.*, 1905, 38, 3673.
- [2] Becker, R.S. and Santiago, A., *J. Amer. Chem. Soc.*, 90, 3654.
- [3] Hart, R.J., Heller, H.G. and Salisbury, K., *J. Chem. Soc., Chem. Comm.*, 1968, 1627.
- [4] Hart, R.J. and Heller, H.G., *J. Chem. Soc. Perkin Trans. I*, 1972, 1321.
- [5] Woodward, R.B. and Hoffmann, R., *The Conservation of Orbital Symmetry*, VCH, Weinheim, 1970.

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الجزء الأول : تحضير ودراسة الخواص اللونية لمركبات ثنائي  
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