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ABSTRACT. Three novel fulgides were synthesized 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[1].

The photochromism of phenyl substituted bis-methylene succinic anhydride “Fulgides” in the solid state was first discovered by Stobbe[1], while the photochromic mechanism of phenyl-substituted fulgides was first postulated by Becker and Santiago[2] and confirmed later by Hart et al.[3] and Hart and Heller[4]. 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[5].

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 $^1$H-nmr spectrum. Table 1 summarises the $^1$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.
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\[ \text{Scheme} \]

\[ \text{Scheme} \]

TABLE 1. $^1$H-NMR data for fulgides 2a-e in ppm.

<table>
<thead>
<tr>
<th>Fulgide</th>
<th>CH$_3$ trans to C = O</th>
<th>CH$_3$ cis to C = O</th>
<th>4-CH$_3$</th>
<th>Aromatic protons</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>1.27</td>
<td>2.30</td>
<td>–</td>
<td>7.17 - 7.50</td>
</tr>
<tr>
<td>2b</td>
<td>1.31</td>
<td>2.31</td>
<td>–</td>
<td>7.04 - 7.26</td>
</tr>
<tr>
<td>2c</td>
<td>1.32</td>
<td>2.31</td>
<td>–</td>
<td>7.10 - 7.36</td>
</tr>
<tr>
<td>2d</td>
<td>1.24</td>
<td>2.28</td>
<td>2.37</td>
<td>7.04 - 7.46</td>
</tr>
<tr>
<td>2e</td>
<td>1.29</td>
<td>2.30</td>
<td>2.41</td>
<td>7.13 - 7.36</td>
</tr>
</tbody>
</table>

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.

*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.

<table>
<thead>
<tr>
<th>Fulgide</th>
<th>λ max/nm</th>
<th>ε a</th>
<th>1,8a - DHNs</th>
<th>λ max/nm</th>
<th>ε a</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>381</td>
<td>4500</td>
<td>3a</td>
<td>493</td>
<td>220</td>
</tr>
<tr>
<td>2b</td>
<td>397</td>
<td>2649</td>
<td>3b</td>
<td>483</td>
<td>170</td>
</tr>
<tr>
<td>2c</td>
<td>398</td>
<td>2905</td>
<td>3c</td>
<td>477</td>
<td>110</td>
</tr>
<tr>
<td>2d/e</td>
<td>400</td>
<td>2884</td>
<td>3d/e</td>
<td>497</td>
<td>180</td>
</tr>
</tbody>
</table>

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. H¹-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 isopropylidenedsuccinate (I)**

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 MgSO₄. 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 ¹H nmr: δ 1.25 and 1.28 (6H, two t, 2 x CH₃), 1.86 (3H, s, CH₃), 2.18 (3H, s, CH₃ cis to C = O), 3.41 (2H, s, CH₂ proton, 4.20 and 4.24 (4H, two overlapped quartet, 2 x CH₂ protons).

**Preparation of fulgides**

**General procedure**

**Diphenylmethylene (isopropylidene) succinic anhydride (2a):** A mixture of diethyl isopropylidenedsuccinate (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 CH₂Cl₂ (2 x 50ml). 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[4] 171.5°C).

[Diphenylmethylene] 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 C₂₀H₁₄O₃F₂ C, 70.58; H, 4.14%), m/z, 340, v_max / 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 C₂₀H₁₄O₃Cl₂ C, 64.34; H, 3.75%); m/z, 342(100), 374(66), v_max / 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 hydrolised 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 C₂₁H₁₈O₃ C, 79.22; H, 5.70%); m/z, 318, v_max / 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

مركبات الفلجاييد ذات التغير اللوني بفاعل الضوء

الجزء الأول: تحضير ودراسة الخواص اللونية لمركبات ثنائي

(4-كلوروفينيل) و (ثنائي فلوروفينيل) ايزوبروپيلدين حامض

السكسينك اللامائي و E و Z (إيزوبروپيلدين -4- ميثيل فينيل)

فينيل ميثيلين أنهيدريد حامض السكسينك

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المستخلص: تم تحضير ثلاثة من الفلجاييد جديدة ودرست خواصها
اللونية قبل التشغيع وبعد التشغيع بالأشعة فوق البنفسجية. الاستبدال في
الموضوع 4- لأحد مجاميع الفينيل أو كلاهما كان له أثر ملحوظ على طول
موجة الامتصاص لكل من الشكل الملون وغير الملون للمركبات

المحضرة.