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New Class of Photochromic Heterocyclic Compounds

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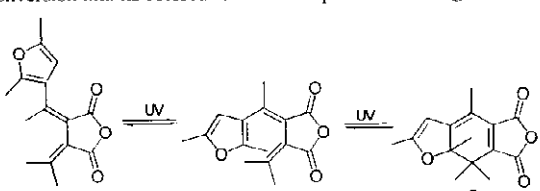
Abstract. Base catalyzed condensation of fulgide (7) with compounds containing active methylene groups such as (8a - 8d) has yielded new class of photochromatic compounds 3-Dicyclopropylmethylene-4-E-[1-(2,5-dimethyl-3-furyl)ethylidene]-5-(4-nitrophenylcyanomethyleneletetrahydrofuran-2-one(10a), 3-Dicyclopropyl-methylene-4-E-[1-(2,5-dimethyl-3-furyl)ethylidene]-5-(3,4-dichl- orophenylcyanomethyleneletetrahydrofuran-2-one (10b), 3-Dicyclopropyl methyl ene-4-E-[1-(2,5-dimethyl-3-furyl)ethylidene]-5-(4-florophenyl-cyanomethylene- terrahydrofuran-2-one (10c) and 3-Dicyclopropylmethylene-4-E-[1-(2,5-dimethyl-3-furyl)ethylidene]-5-(4-chlorophenylcyanomethyleneletetrahydrofuran-2-one (10d). On irradiation with UV light, these compounds photocyclize to compounds having long wavelength absorption bands λ_{max} at (554, 546, 530, 529 nm.) respectively. The spectroscopic and photochromic properties of these compounds were studied.

Keywords: Fulgide; photochromic; color form; succinic anhydride. UV.

Introduction

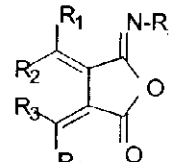
Photochromism has been defined as "a photoinduced transformation of molecular structure, photochemically or thermally reversible, that produces a spectral change, typically, but not necessarily, of visible color" [1]. Although, the photochromic properties of fulgides were discovered more than ninety years ago [2]. Darcy *et al.* [3] synthesized the first thermally stable irreversible photochromic fulgide **1**, which undergoes nearly quantitative conversion into its colored form **2** on exposure to UV light.



1 **2**

Remarkable efforts have been made to increase the wavelength of maximum absorption of the colored form by tailoring the fulgide molecule [4- 8]. Other modifications indcluded the replacement of either the oxygen atom of the carbonyl group or the one in the heterocyclic ring of the anhydride to produce Fulgimides **3** and isofulgimides **4**. These modifications allow the introduction of variable functionally to be attached to the nitrogen, which could be used to produce photochromic polymer [9].

3



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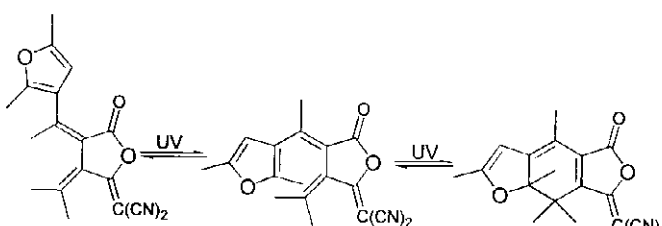
Replacement of the appropriate carbonyl oxygen of the anhydride ring in heterocyclic Z-fulgide **5** with dicyanomethylene group causes a major pathochromic shift >100nm of the long wavelength absorption band of the corresponding fulgides colored forms **6** [10]. (Scheme 1).



5 **6**

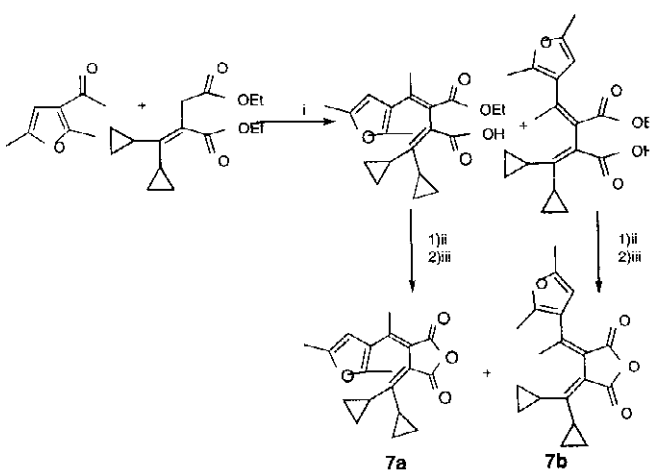
Scheme 1

Results and Discussion

In the present investigation a synthetic attempt leading to new class of photochromic compounds is described. The photochromism of these products have also been reported.

It has been thought that replacement of one of the cyano groups in fulgide **7** by aromatic rings containing electron withdrawing groups may definitely lead to the formation of compounds of strong photochromic activity and of high stability. The (E, Z)- fulgide (**7a** and **7b**) was synthesised via the Stobbe condensation of 3-acetyl-2,3-

dimethylfuran and diethyl dicyclopropyl- methylenesuccinate in the presence of potassium *t*-butoxide in toluene. The fulgide was obtained as a mixture of (E)- and (Z)-isomers (**7a**, **7b**), which where separated by column chromatography and fractional recrystallisation (Scheme 2).



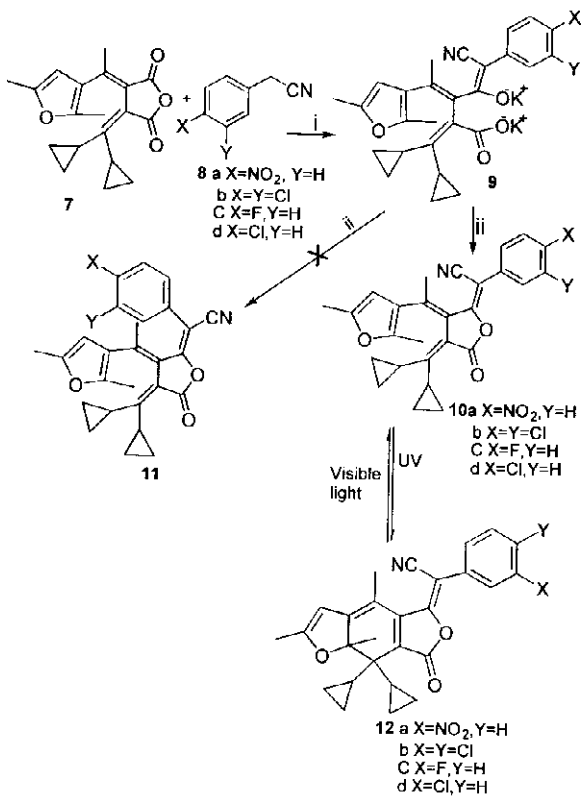
i= *t*-buto-K, toluene. ii = KOH/ EtOH
iii= AcCl, dichloromethane.

Scheme 2

The synthesis consists of adding dropwise a mixture of the E-form of fulgide **7** and the substituted phenylacetonitrile **8a, b, c, d** dissolved in toluene to a stirred suspension of two moles of potassium *t*-butoxide in toluene. In situ cyclization of the resulting disalts **9** with acetyl chloride, afforded compounds **10a, b, c, d** in a 24-67% yield, Scheme 3.

The TLC has shown that a single crystalline product **10** was formed, instead of an expected mixture of two isomers **10 & 11**. It is obvious that the stereochemistry of the E-isomer would make the carbonyl in conjugation with the furylethylidene group more exposed and consequently highly susceptible to nucleophilic attack by the cyanosubstitutedphenyl carbanion, while the other is sterically hindered by the bulky cyclopropyl-groups. Comparison of the ^{1}H NMR spectra of the starting fulgide **7a** and product **10b** have shown that the chemical shifts of the two methyl groups on the furan ring are virtually unchanged (δ 2.2 and δ 2.3). While, the chemical shift of the methyl group cis to the carbonyl of the anhydride has encountered a pronounced upfield shift

from δ 2.7 on the starting fulgide **7a** to δ 1.7 on product Fig. 1. This upfield shift would not have occurred if the nucleophilic attack has occurred on the other carbonyl group. Moreover, the attack on this site is additionally enhanced by conjugation with the adjacent furylethylidene group. This explanation is consistent with an analogous sequence of reactions for the E-fulgide [11].



i=potassium t-butoxide, toluene.
ii=AcCl, DCM.

Scheme 3

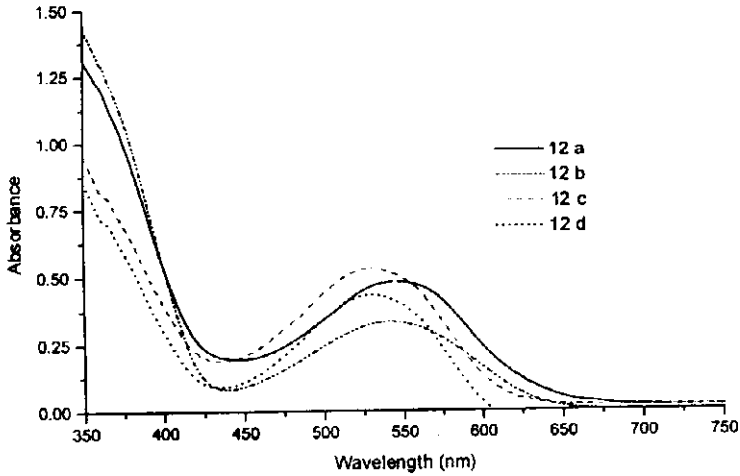


Fig. 1. Absorption spectra of the colored forms (12a– 12d) obtained on irradiation (λ366 nm) of 1x 10^{-4} mol dm^{-3} solutions of the corresponding compounds (10a–10d).

Figure 2 shows the change in the absorption spectra of the colored forms of compounds **12a - 12d** in toluene solution (1X10^{-4} mol dm^{-3}) after irradiation of compounds **10a – 10d** with UV light Scheme 3. Irradiation of compounds **12a - 12d** with visible light induced discoloration.

The photostationary state (pss) for coloration is presumably due to an intramolecular photocyclization of **12a, b, c, d** leading to the formation of the photochromic products with λmax of 554, 546, 530 and 529 nm respectively. The observed shift to higher wavelengths could be considered as a minor pathochromic shift and not a major one. The amount of the shift is not as much as it is expected to account for the effect of introducing an aromatic ring into the system. The diminished effect could only be explained by the assumption that the aromatic ring might not be fully coplanar with the rest of the system.

It could be concluded that the present investigation has established an easy synthetic route to new class of photochromic compounds. It is now becoming feasible to study the effect of substituents on the aromatic ring in relation to the photochromatic properties and stability of these new compounds.

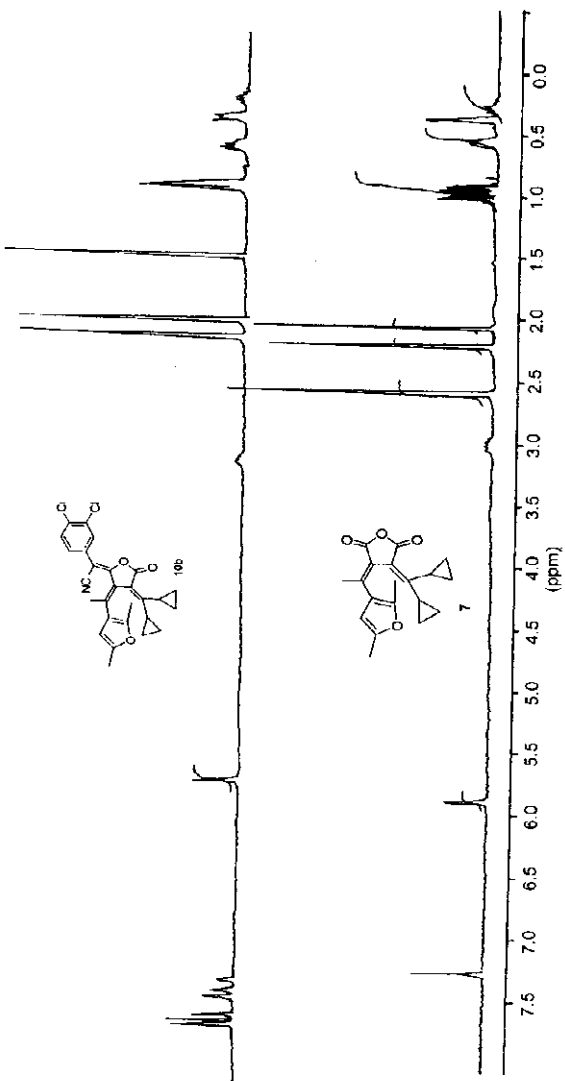


Fig. 2. The ^{1}NMR spectra of E-form fulgide (7) and compound (10b).

Experimental

Melting points were determined on an electrical thermal apparatus and were uncorrected. ^{1}H NMR spectra were obtained for solutions in $CDCl_3$ with TMS as internal standard using a Bruker DPX 400 SF 400.13 MHz spectrometer. Mass spectra were recorded on a Jeol JMS SX102 spectrometer. Microanalyses were carried out using a Perkin Elmer 2400 analyzer.

Dicyclopropylidene(2,5-dimethyl-3-furyl)ethylidenesuccinic anhydride (7).

A mixture of 3-acetyl-2,5-dimethylfuran (34.5 g, 0.25 moles) and dimethyl dicyclopropylmethylene succinate (56.5 g, 0.25 moles) in toluene (50 ml) was added dropwise to stirred solution of potassium t-butoxide (28 g, 0.25 moles). Work-up, gave the half esters as a mixture of the (E) and (Z) isomers. The crude half esters were hydrolysed by boiling (3h) with 10% ethanolic KOH. This was followed by cyclazation with acetyl chloride to give the fulgides, E and Z isomers (26 g, 33% overall yield). The E-isomer was separated by column chromatography. The E-fulgide (7) m.p. 133-134°C. lit [12]. 129°C. ^{1}HNMR: δ 5.90 (1H, s, furyl-4-H); δ 3.01 (1H, M, cyclopropyl); δ 2.59 (3H, s, methyl cis to carbonyl); δ 2.22 (3H, s, Me); δ 2.03 (3H, s, Me); δ 1.05-0.27 (9H, m, cyclopropyl).

General procedure for the preparation of 5-substituted phenyl cyanomethylene-3-4-dimethylenetetrahydrofuran-2-ones.

A mixture of a fulgide (1 mole equivalent) and the active methelene compound (1 mole equivalent) in toluene (5 ml) was added dropwise to a stirred suspension of potassium *t*-butoxide (2 mole equivalent) in toluene (5 ml). When the addition was complete, the reaction mixture was stirred at room temperature for 12 hours. The solvent was then removed. The resulted disalt washed with ether and dried. It was then dissolved in dichloromethane (10 ml) and the solution stirred for (4h) with acetyl chloride (3 ml). The solvent and acetyl chloride were removed under reduced pressure. The residue was dissolved in a minimum amount of dichloromethane and chromatoghraphed on flash silica using a 1:10 mixture of ethyl acetate and petroleum ether (40-60°C) as elutant.

3-Dicyclopropylmethylene-4-E[1-(2,5-dimethyl-3-furyl)ethyl- idene-5-(4-nitrophenylcyanomethylenetetrahydrofuran-2-one (10a).

A mixture of fulgide (7) (1.0 g, 0.003 moles), 4-nitrophenylacetonitrile (8a) (0.5 g, 0.003 moles) and potassium *t*-butoxide (0.9 g, 0.008 moles) was stirred for 12 hours. Work-up gave compound (10a) as greenish powder (0.42 g, 39% yield) from petrol and ether m.p. 161-163°C. (Found: C, 70.60; H, 5.23; N, 6.14%. $C_{27}H_{24}O_5N_2$ requires C, 71.04; H, 5.26; N, 6.14%. m/z, 456. ^{1}HNMR: δ 7.21 (4H, s, aromatic proton); δ 5.97 (1H, s, furyl-4-H); δ 3.80-3.68 (1H, M, cyclopropyl); δ 2.32 (3H, s, methyl cis to carbonyl); δ 2.24 (3H, s, Me); δ 2.16 (3H, s, Me); δ 1.52-0.35 (9H, m, cyclopropyl).

3-Dicyclopropylmethylene-4-E[1-(2,5-dimethyl-3-furyl)ethylidene] 5-(3,4-dichlorophenylcyanomethylenetetrahydrofuran-2-one (10b).

A mixture of fulgide (7) (1.0 g, 0.003 moles), 3,4-dichlorophenylacetonitrile (8b) (0.71 g, 0.003 moles) and potassium *t*-butoxide (0.9g, 0.008 moles) was stirred for 12 hours. Work-up gave compound (10b) (0.350 g, 24% yield) as greenish powder from ethanol m.p. 168-170°C (Found: C, 67.38; H, 4.85; N, 2.72%. $C_{27}H_{23}O_3NCl_2$ requires C, 67.50; H, 4.79; N, 2.92%. m/z, 480. ^{1}HNMR: δ 7.36-7.32 (2H, m, aromatic proton); δ 5.68 (1H, s, furyl-4-H); δ 3.16 (1H, M, cyclopropyl); δ 2.22 (3H, s, methyl cis to carbonyl); δ 2.06 (3H, s, Me); δ 1.54 (3H, s, Me); δ 1.01-0.30 (9H, m, cyclopropyl).

3-Dicyclopropylmethylene-4-E[1-(2,5-dimethyl-3-furyl)ethylidene] 5-(4-florophenylcyanomethylenetetrahydro- furan-2-one (10c).

A mixture of fulgide (7) (1.0 g, 0.002 moles), 4-florophenylacetonitrile (8c) (0.5 g, 0.003 moles) and potassium *t*-butoxide (0.9 g, 0.008 moles) was stirred for 12 hours. Work-up gave compound (10c) as yellow powder (0.35 g, 27% yield) from petrol and ether m. p. 164-165°C. (Found: C, 75.83; H, 5.39; N, 3.46 %. $C_{27}H_{24}O_3NF$ requires C, 75.52; H, 5.60; N, 3.26 %. m/z, 429. ^{1}HNMR: δ 7.45 (4H, m, aromatic proton); δ 5.94 (1H, s, furyl-4-H); δ 3.08 (1H, m, cyclopropyl); δ 2.52 (3H, s, methyl cis to carbonyl); δ 2.24 (3H, s, Me); δ 2.06 (3H, s, Me); δ 1.11-0.28 (9H, m, cyclopropyl).

3-Dicyclopropylmethylene-4-E[1-(2,5-dimethyl-3-furyl)ethylidene] 5-(4-Chlorophenylcyanomethylenetetrahydro- furan-2-one (10d).

A mixture of fulgide (7) (1.0 g, 0.002 moles), 4-Chlorophenylacetonitrile (8d) (0.5 g, 0.003 moles) and potassium *t*-butoxide (0.9 g, 0.008 moles) was stirred for 12 hours. Work-up gave compound (10d) as yellow powder (0.44 g, 31% yield) from petrol and ether m. p. 153-151°C. (Found: C, 72.94; H, 5.48; N, 3.25 %. $C_{27}H_{24}O_3NCl$ requires C, 72.72; H, 5.42; N, 3.14 %. m/z, 445. ^{1}HNMR: δ 7.40 (4H, m, aromatic proton); δ 5.88 (1H, s, furyl-4-H); δ 3.07 (1H, m, cyclopropyl); δ 2.51 (3H, s, methyl cis to carbonyl); δ 2.21 (3H, s, Me); δ 2.03 (3H, s, Me); δ 1.13-0.23 (9H, m, cyclopropyl).

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نوعية جديدة من المركبات الفوتوكرومية غير متجانسة الحلقة

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ملخص البحث. أنتج التكاثف المحفز قاعديا للفولجايد (7) مع مركبات تحتوي على مجموعة ميثلين نشطة (8a-8d)– بعد عمليات نزع الماء والحلقنة – نوعية جديدة من المركبات الفوتوكرومية (10a-10d). تتخلق هذه المركبات ضوئيا عند تعرضها للأشعة فوق البنفسجية إلى المركبات (12a-12d) لتعطي حزما امتصاصية لها أطوال موجيـــة 554، 546، 530 و529 نانوميتر على التوالي. كما تمت دراسة الخواص الطيفية والفوتوكرومية لهذه المركبات.