

**Synthesis and photochromism of
E,E-3,4-Bis-(3,5-dimethoxybenzylidene)succinic anhydride and
its infra red active 2-dicyanomethylene derivative**

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ABSTRACT

The pail yellow fulgide 7 was prepared via two successive stobbe condensation of one equivalent of diethyl succinate and two molar equivalent of 3,5-dimethoxybenzaldehyde. The pail yellow fulgide 7 in both solid and solution turned pink when irradiated with 366 nm light. The fulgide 7 was found to undergoes a Knoevenagel type reaction when condensed with malononitrile under basic condition to give after ring closure the dicyanomethylene derivative 14. The later on irradiation with 366nm gave the infrared active 1,8a-DHN derivative 16. The 1,8a-DHN derivative of fulgide 7 (e.g. 15) showed remarkable positive solvatochromism as the solvent polarity is increased.

INTRODUCTION

Stobbe [1,2] first discovered the photochromism of some phenyl substituted bismethylene succinic anhydrides (fulgides) 1 in the solid state. Later studies showed that the photochromic properties result from photocyclization of these yellow to orange compounds to give red 1,8a-dihydronaphthalene intermediates (1,8a-DHNs) 2 which undergo the reverse process on exposure to white light [3-5]. These stereospecific processes occur in accord with Woodward-Hoffmann rule for pericyclic reaction [6] (Scheme 1).

Organic photochromic compounds, such as fulgides are potential candidates for application in erasable optical information media, much attention have been made to improve their photochromic properties [7]. Previous paper [8] reported that the color of the ring-closed form of fulgides can be altered to deep blue (e.g. λ_{\max} 610 nm) by synthesis of heterocyclic fulgides form 3-pyrryl group. This system is encounter by difficulties in the synthesis of pyrryl fulgides due to the sensitivity of the pyrrol ring to the reaction conditions applied in the condensation. Recently it has been reported that the replacement of one of the carbonyl oxygen by the more powerful electron withdrawing group such as dicyanomethylene to produce novel fulgides derivatives, which on exposure to UV light ring closed to give new photocyclized forms absorbing beyond 600 nm [9-11]. In this paper the synthesis of new symmetrical fulgide 7 and its 2-dicyanomethylene derivative 14 will be investigated.

RESULTS AND DISCUSSION

Synthesis of the fulgide 7

Fulgide 7 was prepared via Stobbe condensation of one mole of diethyl succinate and one mole of 3,5-dihydroxybenzaldehyde using potassium tert-butoxide as a base in toluene at room temperature to form the acid ester 3. The later was reesterified using methanol and acetyl chloride to give the diester 4, which was subjected to another Stobbe condensation with the other mole of 3,5-dihydroxybenzaldehyde to give the acid ester 5 which was hydrolyzed using alcoholic potassium hydroxide to give the diacid 6. The diacid 6 was dehydrated to give Fulgide 7 as yellow needles (Scheme 2). The fulgide 7 was obtained exclusively as E,E-isomer as follows from its $^1\text{H-NMR}$ spectrum which showed a singlet at 3.60 ppm assigned to the four methoxy groups, two doublets, one at 6.0 ppm and the other at 6.30 ppm assigned to the aromatic hydrogens, and a two proton singlet at 7.83 ppm assigned to the olefinic protons shielded by the aromatic rings.

Synthesis of dicyanomethylene derivative 14

Recently it has been reported that, one carbonyl group of the succinic anhydride moiety can be substituted by the more powerful electron withdrawing group such as the dicyanomethylene group. [9-11]

In unsymmetrical fulgides such as 8, the carbonyl group in conjugation with the aryl group is more susceptible to nucleophilic attack by nucleophile such as dicyanomethane anion and only compound 9 was obtained, as confirmed by x-ray single crystal analysis [12]. This process is governed by two factors, the electronic vs the steric factors. The electronic favor the attack to take place on the carbonyl group in conjugation with the aromatic ring to form for example

compound 9. On the other hand the steric effect favor the attack to be on the less hindered carbonyl which is the carbonyl adjacent to the isopropylidene group to form compound such as 10. This indicate that the aromatic group is more likely to be planer with the anhydride moiety so the electronic density can be migrated more easily to the carbonyl group adjacent to it. When compound 9 was irradiated with UV light an electrocyclization took place and compound 11 was formed. The cyclized form 11 did not show large bathochromic shift, because the powerful dicyanomethylene group is not in conjugation with the aromatic ring in the 1,8a-DHN derivative 11. On the other hand if the dicyanomethane anion would attack the other carbonyl group of fulgide 8 to give the dicyanomethylene 10, then on irradiation with UV light the cyclized form 12 would expect to show large bathochromic shift compared to the corresponding cyclized form of the original fulgide 8. To overcome the problem of preferential attack, a symmetrical fulgide was required and for this reason, the fulgide 7 was prepared. The dicyanomethylene derivative 14 was prepared by condensation of fulgide 7 and dicyanomethane anion generated in situ by adding diethylamine to malononitrile in THF at room temperature, then the fulgide solution was added the salt 13 formed was cyclized to give the dicyanomethylene derivative 14 as pail yellow crystals. The later was obtained as *E,E*-isomer as established by its ¹H-NMR spectrum, which showed two singlets at 8.33 and 7.82 ppm attributed to the olefinic protons in conjugation with dicyanomethylene and carbonyl respectively. The introduction of the dicyanomethylene group causes low fields shift of the adjacent olefinic protons and left the other proton chemical shift unchanged.

Photochromism of fulgide 7 and its dicyanomethylene derivative 14

On irradiation at 366nm of fulgide 7 in both solid and solutions, a yellow to red coloration was observed. The red color formed is attributed to the formation of the dihydronaphthalene (DHN) derivative (15, X=O). The cyclization took place without any preferential between the two aromatic groups as shown in scheme 4. The original color of fulgide 7 can be restored on exposure to whit light.

Likewise the dicyanomethylene derivatives (14) gave upon irradiation at 366nm similar cyclization to form the infrared active 1,8a-dihydronaphthalen derivative (1,8a-DHN) 16 which has absorption maximum at 676nm. The cyclization took place on the aromatic group not in conjugation with the dicyanomethylene moiety as evidenced by the large bathochromic shift of the cyclized form 16 rather than forming 17 which is expected to absorb as the cyclized form of fulgide 7. The introduction of the dicyanomethylene group resulted in large bathochromic shift of the colored form of compounds 16 compared to the cyclized form of the unsubstituted fulgide 15. The original color of the dicyanomethylene 14 can be restored on exposure to whit light.. Table 1 summarizes the electronic spectral properties of fulgide 7 and its dicyanomethylene 14 in toluene before and after irradiation at 366nm.

Solvatochromism of fulgide 7 and its 1,8a-DHN derivative 15

The uv visible spectra of fulgide 7 and its cyclized form 15 were investigated in four different solvents, and the data are summarized in table 2. As the solvent's polarity increased the absorption maxima of both the colored and the uncolored forms are red shifted. This may be due to the stability of the excited state of both forms as they received large contribution from the resonance hybrid 18 (Scheme 5).

EXPERIMENTAL

Melting points were recorded on a Thomas-Hoover capillary melting apparatus without correction. IR spectra were taken as KBr disk on a Nicolet Magna 520 FTIR spectrometer, ^1H NMR were recorded in CDCl_3 on a Bruker DPX 400 MHz spectrometer using TMS as internal standard. UV-visible spectra were recorded on a Shimadzu 260 spectrometer for solutions.

Dimethyl 2-(E)(3,5-dimethoxybenzylidene)succinate 4.- A mixture of dimethyl succinate (9.0 g, 0.09 mol) and 3,5-dimethoxybenzaldehyde (20 g, 0.12 mol) in dry toluene (150 ml) was added dropwise to a well stirred solution of potassium tert-butoxide (30 g, 0.26 mol) in dry toluene (150 ml) at 20°C . After the addition was completed the stirring was continued at 20°C for further 20 hrs. The solvent was removed in vacuo, the residue was dissolved in water (375 ml), extracted with diethyl ether (2x50 ml) and the aqueous layer was acidified using aqueous hydrogen chloride (6 M, 100 ml). The residual acid ester was extracted with diethyl ether (3x100 ml), dried (Na_2SO_4) and filtered to give the acid ester 3 as a brown gum (16g, 93%). The crude acid ester 3 (16g) was dissolved in methanol (100 ml), acetyl chloride (20 ml) was added dropwise at 20°C , the mixture was heated at reflux for 5 hrs, then the solvent removed in vacuo and the residual gum was distilled to give the diester 4 as deep yellow semisolid (16 g, 88%), m.p. 80°C . Found: C, 61.02; H, 6.25%. $\text{C}_{15}\text{H}_{18}\text{O}_6$ requires C, 61.24; H, 6.12%. δ_{H} 7.85 (1H, s, olefinic proton), 6.4 (1H, d, J 2.3 Hz), 6.01 (2H, d, J 2.3 Hz), 4.10, 4.05 (6H, s, 2x CH_3O), 3.64 (6H, s, 2x CH_3O), 3.20 (2H, s, CH_2).

E,E-2,3-Bis-3,5-(dimethoxybenzylidene)succinic acid 6.- Dimethyl 2-(E)(3,5-dimethoxybenzylidene)succinate 4 (16g, 0.054 mol) and 3,5-dimethoxybenzaldehyde (9.0g, 0.054 mol) in toluene (100 ml), was added dropwise to a suspension of potassium tert-butoxide (7.15g, 0.064 mol) in toluene (150 ml) with stirring at 20°C . After the addition was completed the stirring was continued for 12 hrs at 20°C , the solvent was evaporated in vacuo, the residue was dissolved in water (100 ml) and acidified with aqueous hydrogen chloride (6 M, 100 ml). The residual oily product 5 was extracted with diethyl ether (3x50 ml) and was dissolved in alcoholic KOH (100 ml, 10%) heated at reflux for 8 hrs, then the solvent removed in vacuo. The residue was dissolved in water (100 ml) and acidified with aqueous hydrogen chloride (6 M, 100 ml). The liberated di-acid was extracted into ether (2x50 ml), dried (Na_2SO_4) and filtered. The solvent was removed to give the diacid 6 as dark yellow oil, which was dissolved in diethyl ether and left to crystallize. The diacid 6 was obtained as white crystals (12.58g, 49% overall yield) mp $>300^\circ\text{C}$. Found: C, 63.55; H, 5.46%. $\text{C}_{22}\text{H}_{22}\text{O}_8$ requires C, 63.78; H, 5.31%.

E,E-Bis-(3,5-dimethoxybenzylidene)succinic Anhydride 7.- The diacid 6 (12g, 0.029 mol) was dissolved in dichloromethane (25 ml) and to this mixture was added acetyl chloride (30 ml) dropwise with stirring at 0°C , and the mixture then stirred at 20°C for six hrs. The excess acetyl chloride was removed in vacuo and the crude product was chromatographed on silica gel eluting with diethyl ether: light petrol (1:1). The pure E,E-fulgide was crystallized from ethanol as deep yellow crystals (4.5g, 18% overall yield), mp $180\text{--}182^\circ\text{C}$. Found: C, 66.68; H, 5.58%. $\text{C}_{22}\text{H}_{20}\text{O}_7$ requires C, 66.68; H, 5.05%. δ_{H} 7.83 (1H, s, olefinic proton), 6.3 (1H, d

, J 2.4 Hz, para aromatic protons), 6.00 (2H, d, J 2.4 Hz, ortho aromatic protons, 3.6 (6H, s, 2xCH₃O); ν_{\max} 1822(C=O), 1766 (C=O) cm⁻¹.

E,E-3,4-Bis(3,5-dimethoxybenzylidene)-2-Dicyanomethylene-tetrahydrofuran-5-one 14.- Diethylamine (0.58g, 7.94 mmol) was added dropwise with stirring to a solution of E,E-Bis-(3,5-dimethoxybenzylidene)succinic Anhydride 7 (1.50g, 3.79 mmol) and malononitrile (0.26g, 3.93 mmol) in THF (20 ml) at 0 °C. The mixture was then stirred at 0 °C for 6 hrs, diethyl ether (15 ml) was added, the disalt 13 was not isolated, the crude product was dissolved in dichloromethane (20 ml) and cyclized by stirring with acetyl chloride (15 ml) at 20 °C for 12 hrs. The solvent and excess acetyl chloride were removed in vacuo, and the residual was chromatographed on silica gel eluting with a 3:7 mixture of ethyl acetate and light petroleum to give the dicyanomethylene 14 as yellow crystals (0.87g, 52% yield), m.p. 200-201°C from ether / light petroleum. Found: C, 67.82; H, 4.58; N, 6.33%. C₂₃H₂₀O₄N₂ requires C, 67.58; H, 4.50; N, 6.30%. δ_{H} 8.33 (1H, s, olefinic proton cis to C(CN)₂), 7.82 (1H, s, olefinic proton cis to C=O), 6.34 (1H, dd overlap, J 2.23 Hz), 6.27 (1H, sdd overlapped, J 2.23 Hz), 6.0 (2H, d, J 2.18 Hz), 5.98 (2H, d, J 2.18 Hz), 3.64 (6H, s, 2x CH₃O), 3.62 (6H, s, 2xCH₃O). λ_{\max} 354 nm (log ϵ 4.26); ν_{\max} 2306 (CN), 1819 (CO) cm⁻¹.

Photochemical reactions of fulgide 7 and the dicyanomethylene derivative 14-. A toluene solution of the fulgide or the dicyanomethylene derivative (c.a. 10⁻⁴ M) was irradiated with 366 nm from a 250 W mercury discharge lamp (type ME/D Thorn Lighting) with a filter (type OX1 change Pilkington). The irradiation was continued while monitoring the absorption of the new visible band formed until no absorption change was observed.

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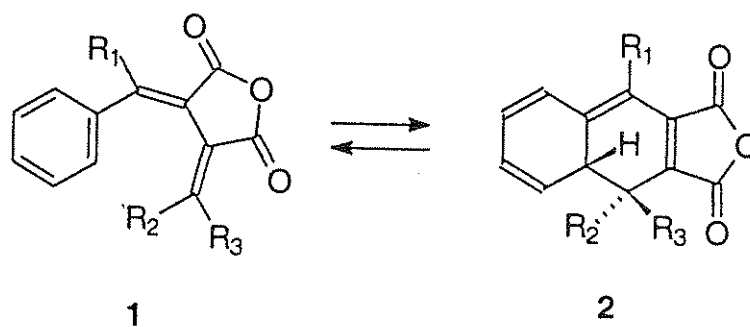
Table 1. Uv-visible Spectral Data of Fulgide 7 and its dicyanomethylene derivative 14 before and after irradiation at 366nm

Compound No.	λ_{\max} (nm)	ϵ_{\max} (L.mol ⁻¹ .cm ⁻¹)
7	353	12589
15	530	5000
14	402	18197
16	676	6500

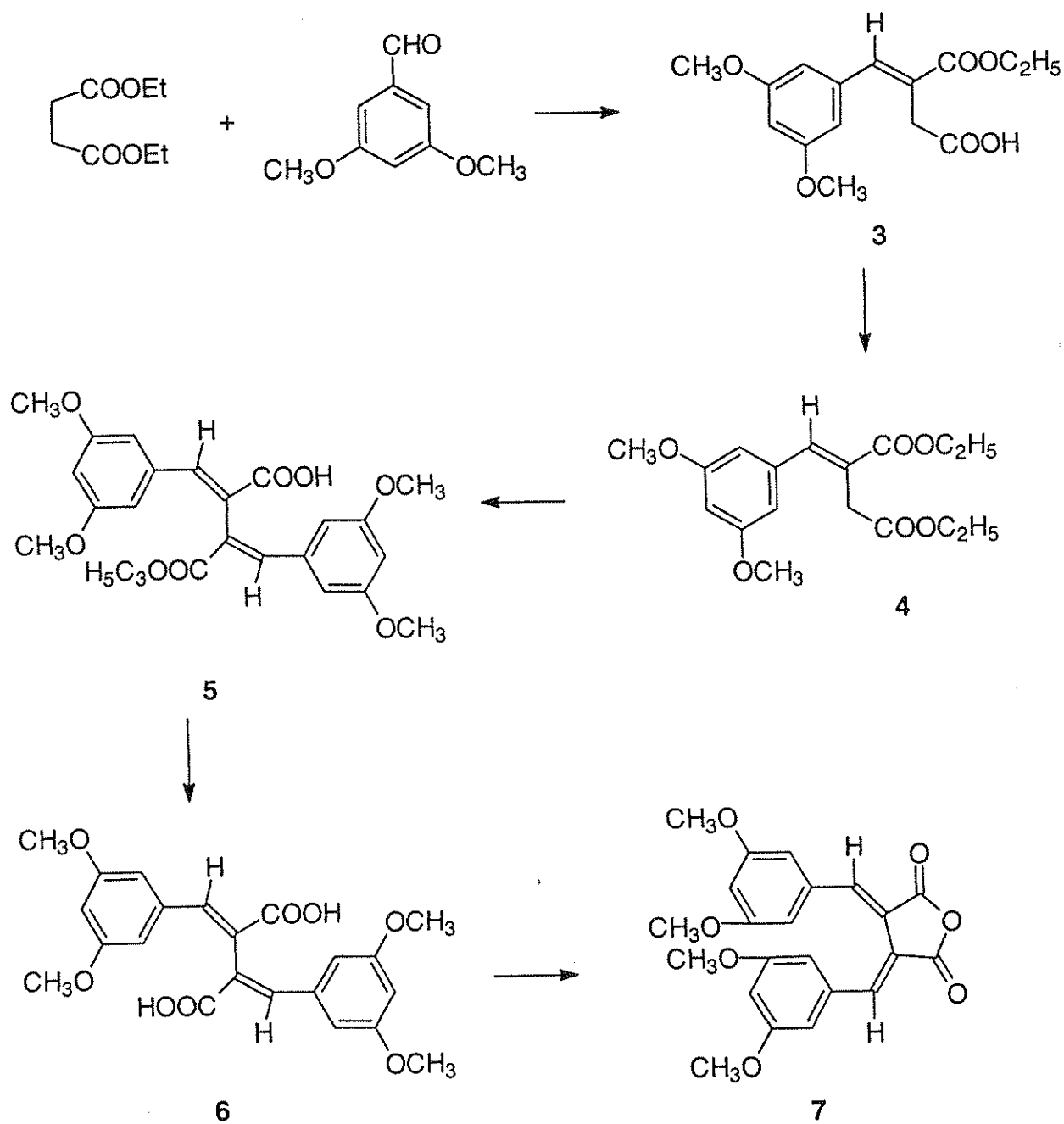
Table 2. UV-Visible Spectral Data of fulgide 7 and its 1,8a-DHN 15 in various solvents

Solvent	Permittivity at 20 °C	λ_{\max} (nm) Fulgide 7	λ_{\max} (nm) 1,8a-DHN 15
Hexane	1.89	346	506
Toluene	2.38	353	530
CHCl ₃	4.80	354	558
DCM*	9.08	354	564

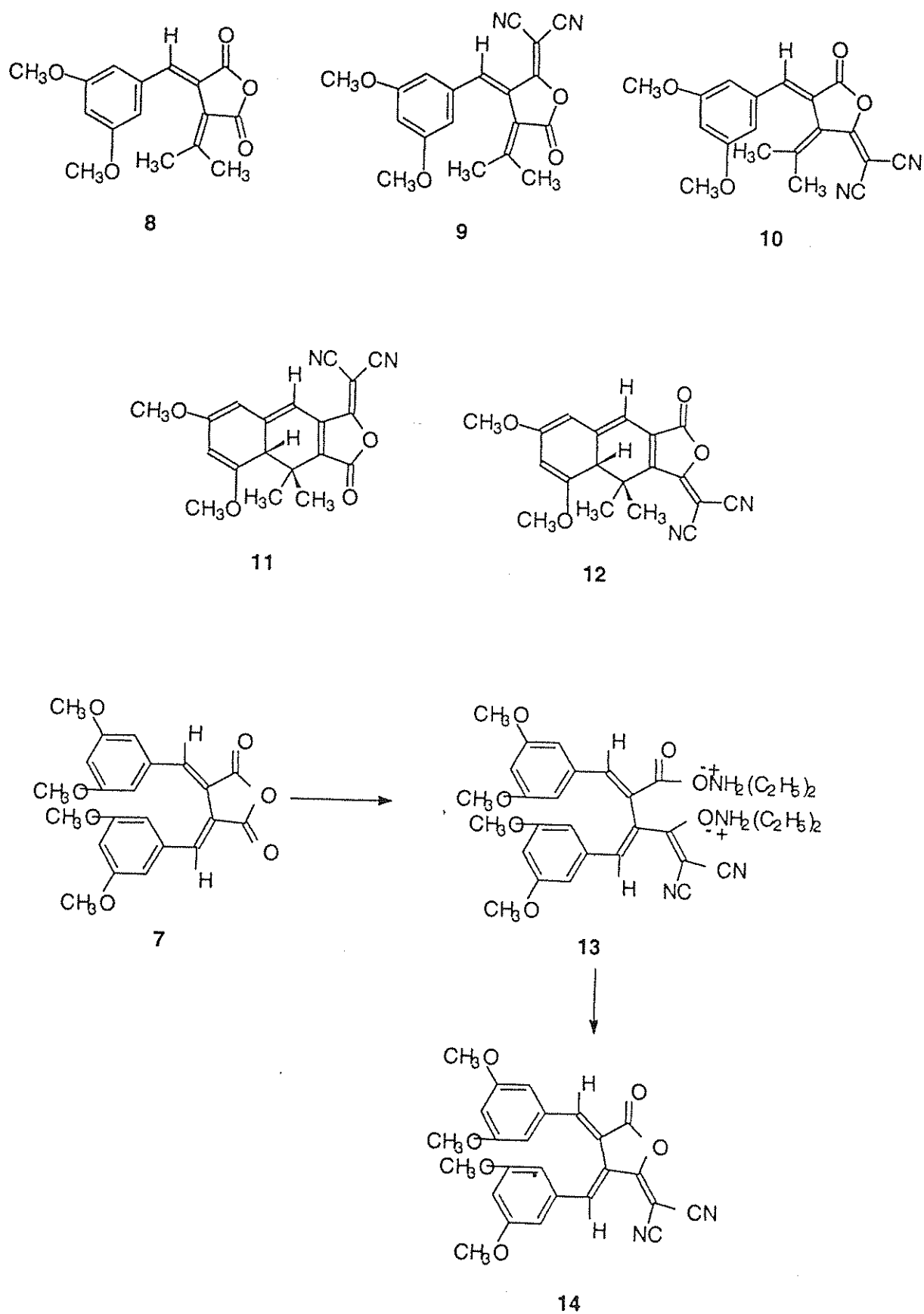
- DCM denotes dichloromethane

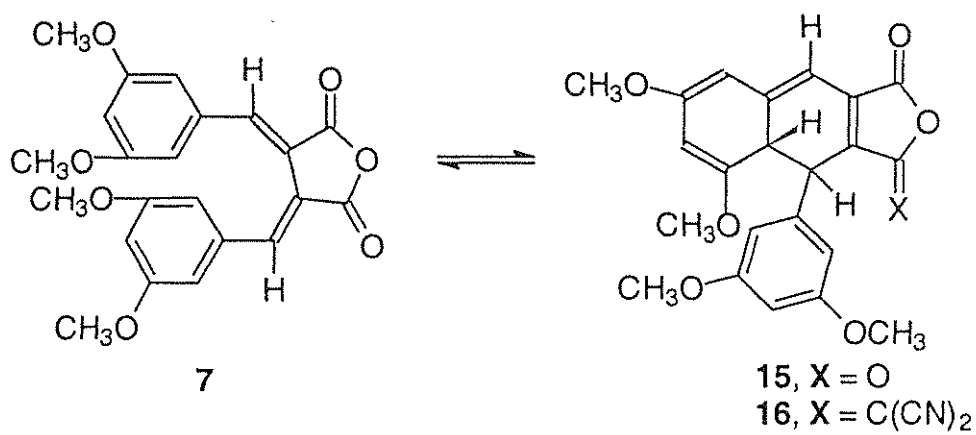


Scheme 1

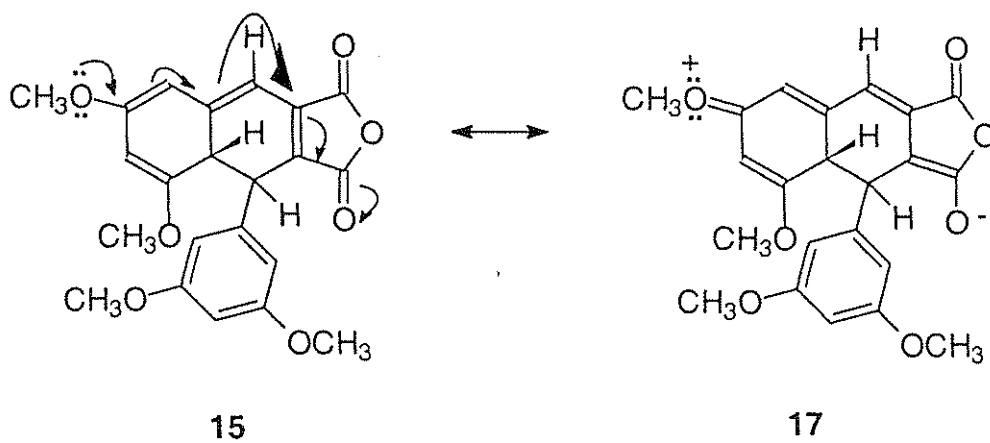


Scheme 2





Scheme 4



Scheme 5