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FULGIDES AND FULGIMIDES FOR PRACTICAL APPLICATIONS

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Abstract A new class of photochromic compounds called isofulgimides is described and their photochromic and chemical transformations discussed. Their potential in commercialization of these photochromes is also indicated.

INTRODUCTION

Fulgides^{1,2} are a well known class of photochromic compounds which have the following properties which make them suitable for commercial applications:-

- (1) Complete thermal stability at ambient temperatures.
- (2) High conversion of near colourless form into the more highly coloured form on irradiation with ultraviolet light.
- (3) High quantum efficiencies for forward and reverse reactions.
- (4) Good fatigue resistance.
- (5) Straightforward synthetic methods suitable for large-scale synthesis.

The name "fulgimide" had been introduced to describe the photochromic imides based on fulgides³. However, the number of investigations of fulgimides containing heteroaromatic substituents which gave the photochromic properties suitable for commercial applications were limited due to a lack of convenient synthetic route.

PREVIOUS SYNTHETIC ROUTES TO FULGIMIDES

Goldschmidt⁴ (1957) had reported that bisfluorenylidenesuccinimide could be synthesized by treating the corresponding fulgide with ammonia to give the succinamic acid, esterification with diazomethane to methyl bisfluorenylidenesuccinamate and finally cyclization with sodium methoxide in methanol. We had demonstrated⁵ that this method gave good results for fulgides with furyl substituents which gave good photochromic properties. These fulgimides exhibited photochromic properties similar to their corresponding fulgides. Smets and Deblauwe⁶ had alkylated these N-hydrogen fulgimides with p-bromomethylstyrene to give fulgimides with a styrene functional group which could be formed into photochromic styrene co-polymers.

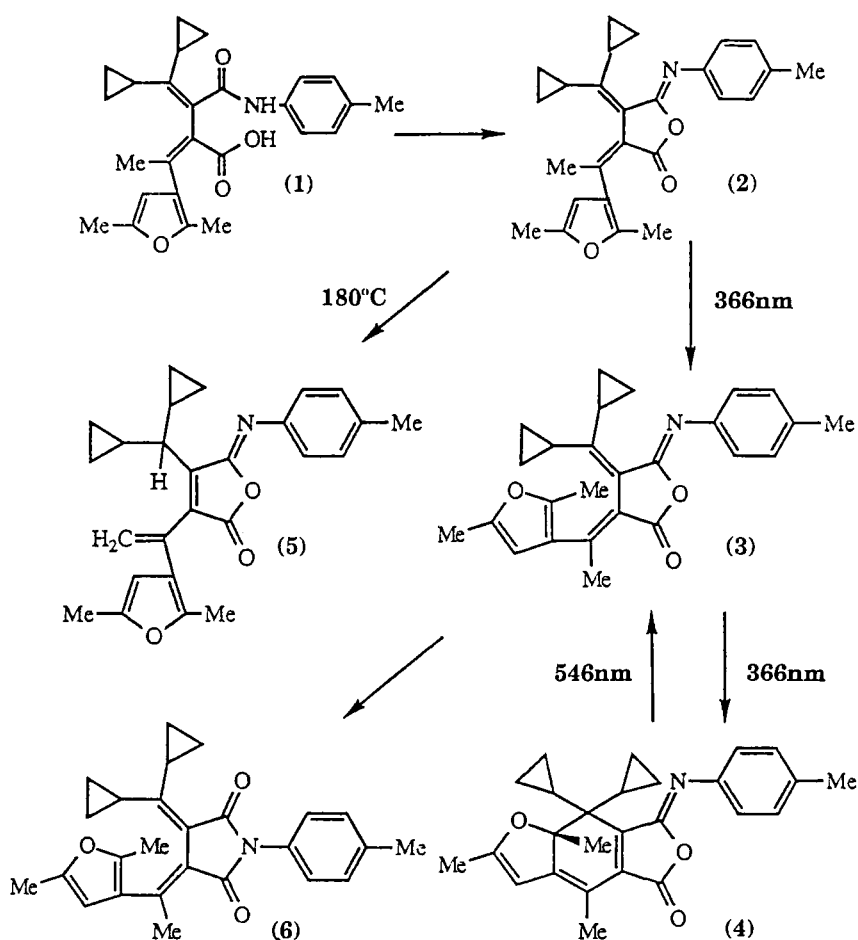
The use of dehydrating agents normally associated with fulgide/fulgimide synthesis (ie acetyl chloride or acetic anhydride) to convert succinamic acids derived from fulgides with desirable photochromic properties but having acid sensitive functional groups (ie furyl and cyclopropyl) had given low yields of fulgimides and was limited to relative simple functionality on the amine precursors. Photochromic Langmuir-Blodgett films⁷ and liquid crystals⁸ based on this type of chemistry had been reported.

ISOFULGIMIDES

We envisaged that useful functionalisation of fulgimides could be achieved by cyclization of succinamic acids using the mild, neutral dehydrating agent dicyclohexylcarbodiimide. When the succinamic acid (1) was reacted with dicyclohexylcarbodiimide a photochromic compound was obtained which when irradiated with ultraviolet light gave a coloured form with a slight hypsochromic shift with respect to the coloured form of the fulgide instead of the slight bathochromic shift normally observed with N-aryl fulgimides. In the synthesis of

succinimides, maleimides and phthalimides the so called isoimides, in which one carbonyl had been replaced by an imine group had often been isolated.^{9,10,11} An x-ray crystallographic study¹² confirmed that the isoimide (2) had been formed and the name "isofulgimide" was introduced for this new class of photochromic compounds.

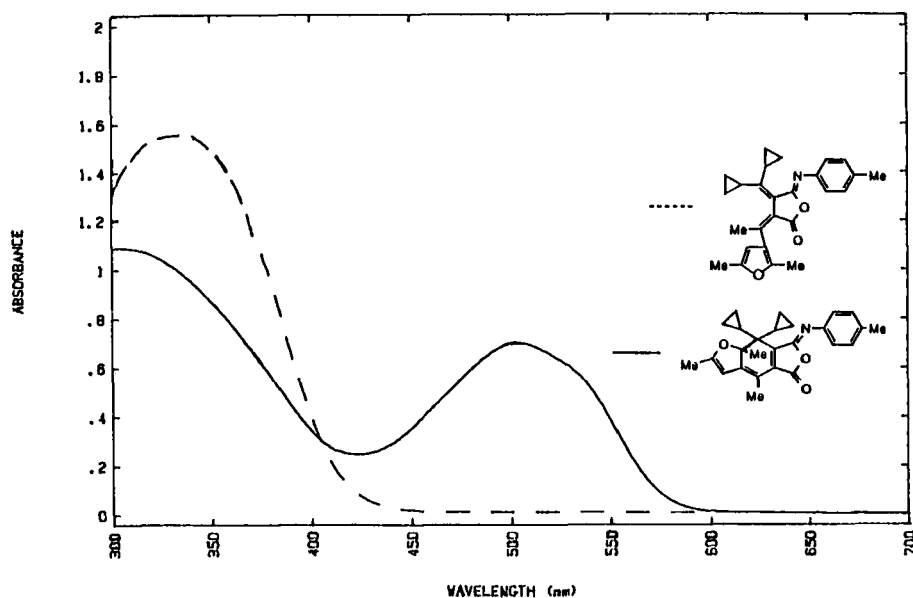
Other conditions that were found to convert succinamic acids into isofulgimides included carbon tetrachloride-triphenylphosphine, diethyl diazocarboxylate-triphenylphosphine or N,N-carbonyldiimidazole. These all have mild, neutral conditions that avoid side reactions such as acid catalysed polymerization and hence give good yields. The presence of acid or nucleophiles also causes further rearrangement to fulgimides.



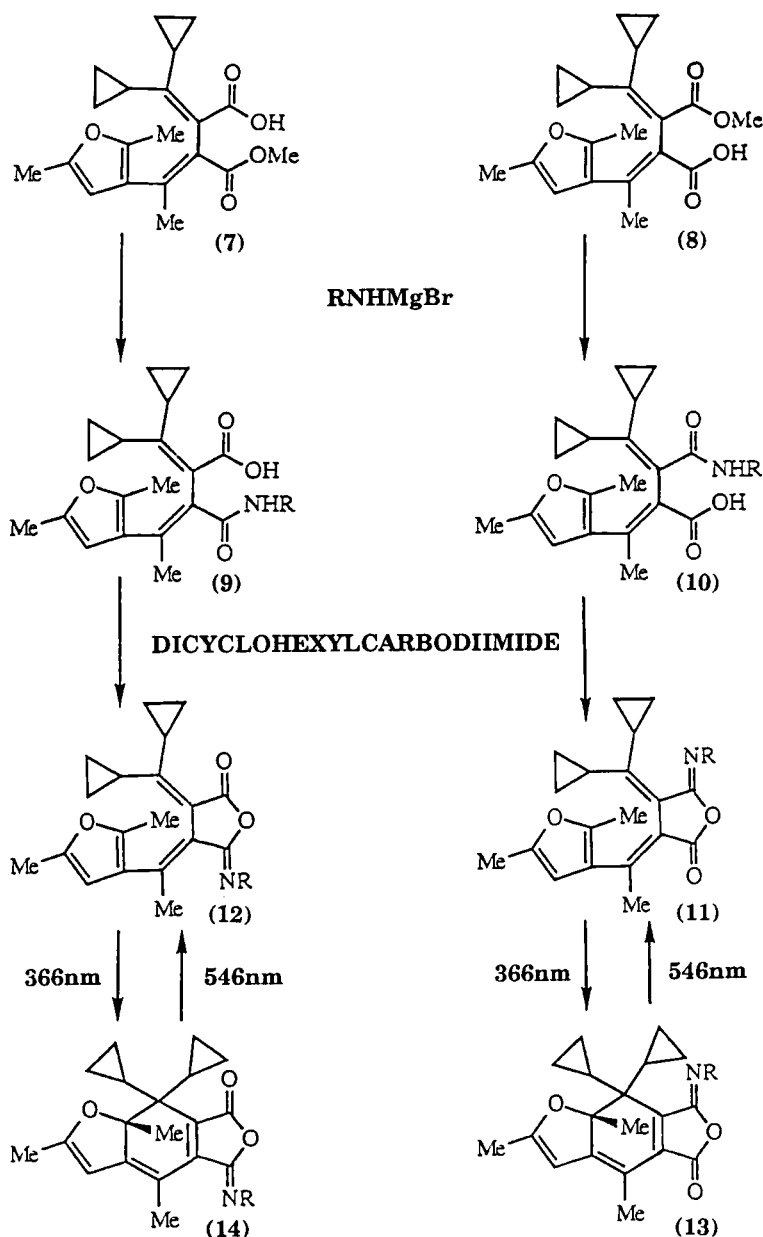
On irradiation with 366nm light the (Z)-isofulgimide (2) isomerized into the (E)-isofulgimide (3) which underwent a photochemical cyclization to give the coloured 7,7a-dihydrobenzofuran (4) (λ_{max} 502nm in toluene). When this was irradiated with visible light the (E)-isofulgimide (3) was regenerated. When the (Z)-isofulgimide (2) was heated at 180°C (CDCl₃ sealed tube) it underwent a [1,5]-hydrogen shift to give the isomaleimide (5).

Although the isofulgimide (3) did not convert into the fulgimide photochemically or thermally, when exposed to acid or nucleophiles the fulgimide (6) was formed.

The ultraviolet/visible spectra for (2) and (4) are shown below.



Both isomers of the half-esters (7) and (8) were readily available from the Stobbe condensation¹³ and these could be reacted with magnesium amide nucleophiles (from an amine and Grignard reagent base) to give the regioisomeric succinamic acids (9) and (10). When these were cyclized with dicyclohexylcarbodiimide both isomers of the isofulgimides (11) and (12) were formed.



The isofulgimide (11) which has the imine group on the opposite side of the succinic ring as the furyl group so that the nitrogen forms part of the conjugated main chromophore in the coloured form (13) has been termed the alpha-isofulgimide while the other isomer (12) has been called the beta-isomer.¹⁴

Both the alpha and the beta isofulgimides (11), $R=N(\text{Me})\text{Ph}$ and (12), $R=N(\text{Me})\text{Ph}$ were studied. These both have quantum yields for colouring similar to the parent fulgide while their coloured forms have quantum yields for bleaching similar to the coloured form (15). However, these coloured forms (13), (14), $R=N(\text{Me})\text{Ph}$ both have large hyperchromic effects while the alpha-isomer (13), $R=N(\text{Me})\text{Ph}$ shows a small hypsochromic effect while the beta-isomer (14), $R=N(\text{Me})\text{Ph}$ shows a large hypsochromic effect. The data for toluene solutions for these isofulgimides as well as for the coloured forms for the corresponding fulgide (15) and fulgimide (16) is shown in table 1.

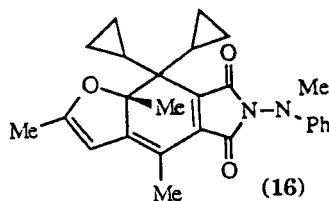
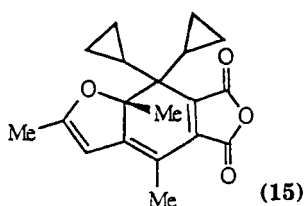


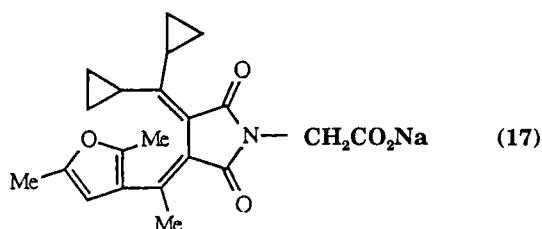
Table 1

COMPOUND	(13)	(14)	(15)	(16)
λ_{max} nm	497	438	502	527
ϵ_{max} dm ³ mol ⁻¹ cm ⁻¹	16,300	21,800	7,900	6,500
Fatigue resistance cycles	14	12		24

The fatigue resistance for the isofulgimides are slightly less than for the fulgimides.

FULGIMIDES

Although the above isofulgimides had exhibited a range of interesting photochromic properties their reduced fatigue resistance had made them less attractive for commercial applications. However, using the described methods the water-soluble fulgimide (17) was synthesized.



This fulgimide could then be used in water-based technology which offers the advantages of being more attractive to large scale use due to the absence of harmful organic solvents and also additives with low oxygen permeability (polyvinylalcohol, gelatin) can be incorporated and these then construct photochromic films with markedly increased fatigue resistance. Development in this area continues.

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