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# A convenient method for conversion of the *Z*-isomer to the *E*-isomer from a mixture containing both isomers of fulgides

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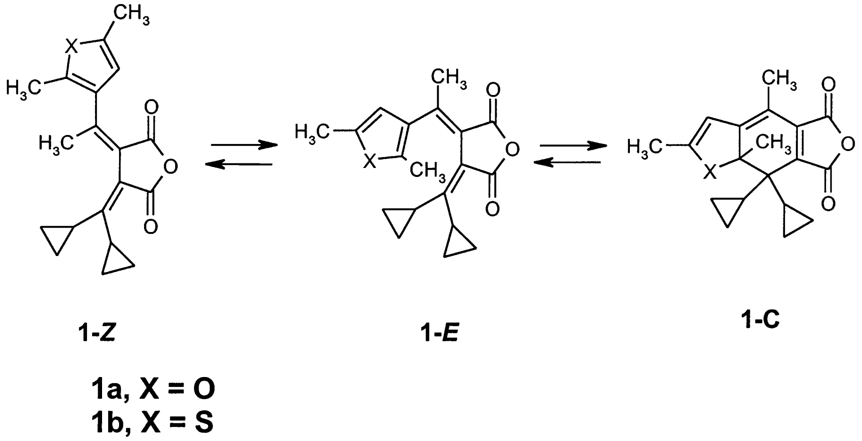
**Abstract**—A new method for the conversion of the *Z*-isomer of unsymmetrical substituted bis-methylenesuccinic anhydrides, ‘fulgides’, to their geometrical *E*-isomers was achieved by heating the *Z*-isomer under reflux or a mixture of both isomers in pyridine to give the *E*-isomer in near quantitative yield. © 2002 Elsevier Science Ltd. All rights reserved.

Fulgides are potential candidates for many advanced technology applications.[1–4] The development of a reversible optical information storage medium based on photochromic organic compounds, as suggested by Hirshberg,[5] became a potential commercial reality with the discovery of the first thermally-stable fatigue-resistant near colorless photochromic fulgides, which undergo near quantitative conversion into their colored forms on exposure to UV light.[6] It is known that if the ketone used in a Stobbe condensation, which is the normal procedure for the synthesis of fulgides, is unsymmetrical such as 3-acetyl-2,5-dimethylfuran, the condensation products, and hence the fulgides formed, will be obtained as a mixture of both possible geometrical isomers **1-*E*** and **1-*Z***, respectively. The formation of both isomers obviously leads to a lower yield of the desired *E*-isomer, which is the only isomer that undergoes ring closure to give the 7,7a-dihydrobenzofuran derivative **1-C** (Scheme 1). In this communication we report a new method for the conversion of a mixture containing both *E* and *Z* isomers to the desired *E*-isomers in near quantitative yield (Table 1).

Thus, when a 1:1 mixture of both isomers, **1-*E*** and **1-*Z***, of a fulgide was heated in pyridine, a green coloration was observed. After treating the solution with hydrochloric acid the green color faded and pale yellow crystals of the *E*-isomer were isolated. The mechanism which we suggest for this conversion is believed to be through the formation of the green zwitterion **2**



**Scheme 1.**

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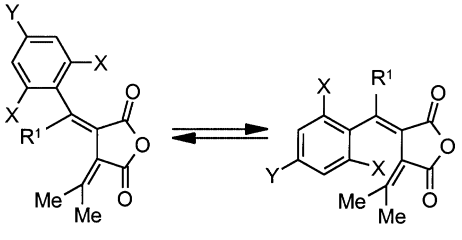
**Table 1.** $^1$H NMR data of the *E*- and the *Z*-isomers of fulgide **1a**

| Assignment | *E*-Isomer | *Z*-Isomer |
|---|---|---|
| 2-Me | 2.59 | 2.44 |
| 5-Me | 2.08 | 2.18 |
| Ethylidene-Me | 2.22 | 2.17 |
| Furyl-4-H | 5.90 | 5.97 |
| Cyclopropyl-bridgehead-H (1H, m) | 3.01 | 3.17 |
| Cyclopropyl-H (9H, m) | 0.40–1.15 | 0.4–1.40 |

**Table 2.** $^1$H NMR data of the *E*- and the *Z*-isomers of fulgide **1b**

| Assignment | *E*-Isomer | *Z*-Isomer |
|---|---|---|
| 2-Me | 2.21 | 2.19 |
| 5-Me | 2.40 | 2.42 |
| Ethylidene-Me | 2.63 | 2.35 |
| Thionyl-4-H | 5.50 | 6.53 |
| Cyclopropyl-bridgehead-H (1H, m) | 3.04 | 3.11 |
| Cyclopropyl-H (9H, m) | 1.21–0.30 | 1.20–0.50 |

(Scheme 2), which permits the rotation of the furyl ring around the single bond. Intermediate **2** in the presence of hydrochloric acid decomposes to give only the *E*-isomer in very high purity. The $^1$H NMR spectrum of the *E*-isomer showed a singlet at $\delta$ 2.59 ppm for the methyl group at C-2, similarly the *Z*-isomer showed the same methyl singlet at $\delta$ 2.44 ppm. This transformation of the *Z* to the *E* isomer was also observed for some other heterocyclic fulgides, for example **1b** derived from thiophene. Tables 1 and 2 summarize the $^1$H NMR data of both geometric isomers of fulgides **1a** and **1b**. This transformation was also found to take place in the case of simple aromatic fulgides such as fulgides **3a**–**c** (Scheme 3). Table 3 summarizes the $^1$H NMR data of both *E* and *Z* isomers of fulgides **3a**–**c**.



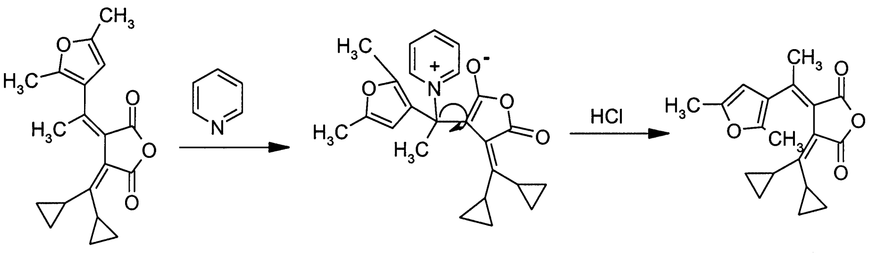
**3-*Z*** **3-*E***

**3a,** R$^1$ = H , X =Y =Me
**3b,** R$^1$ = Me , X = Y = H
**3c,** R$^1$ = Me , X = H ,Y =MeO

**Scheme 3.**

## Experimental

A solution of a 1:1 mixture of fulgide **1a** (1.0 g) and anhydrous pyridine (20 ml) was refluxed for 4 h, cooled and poured into dilute hydrochloric acid (5 M). The aqueous solution was extracted with diethyl ether, the organic layer was washed with water, dried ($MgSO_4$) and the solvent evaporated. The residue was recrystallized from 3:7 chloroform–petroleum ether (40:60) to give the pure *E*-isomer). Yield ( 0.95 g), mp 129°C, $^1$H NMR (see Table 1).



**1a-*Z*** **2** **1a-*E***

**Scheme 2.**

**Table 3.** $^1$H NMR data of the *E*- and *Z*-isomers of fulgides **3a**–**c**

| Compound no. | R$^1$ | Me-2 | Me-3 | Aromatic-H | Other |
|---|---|---|---|---|---|
| **3a**-***Z*** | 7.52 | 2.34 | 2.62 | 6.92 | 2.16, 2.39 3 × Me |
| **3a**-***E*** | 7.77 | 1.22 | 2.37 | 8.84 | 2.07,2.23 3 × Me |
| **3b**-***Z*** | 2.38 | 1.99 | 2.18 | 7.2–7.4 | |
| **3b**-***E*** | 2.64 | 1.01 | 2.12 | 7.2–7.4 | |
| **3c**-***Z*** | 3.37 | 1.98 | 2.14 | 7.15–7.37 | 3.73 MeO |
| **3c**-***E*** | 2.61 | 1.11 | 2.14 | 6.82–7.2 | 3.76 MeO |

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