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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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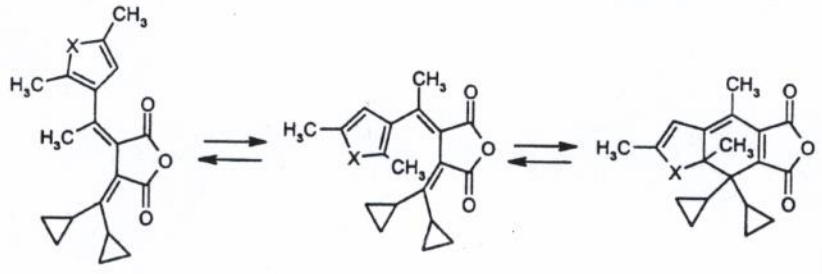
Abstract—A new method for the conversion of the *Z*-isomer of unsymmetrical substituted bis-methylenesuccinic anhydrides, 'fulgides', to their geometrical *E*-isomers was achieved by heating the *Z*-isomer under reflux or a mixture of both isomers in pyridine to give the *E*-isomer in near quantitative yield.

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**



1-*Z* **1-*E*** **1-C**

1a, X = O
1b, X = S

Scheme 1.

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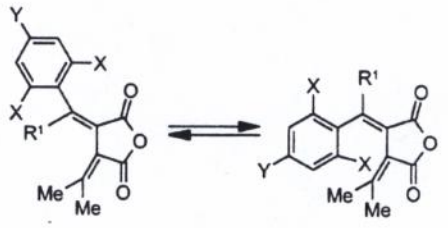
Table 1. ^{1}H NMR data of the *E*- and the *Z*-isomers of fulgide **1a**

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 δ 2.59 ppm for the methyl group at C-2, similarly the *Z*-isomer showed the same methyl singlet at δ 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**.



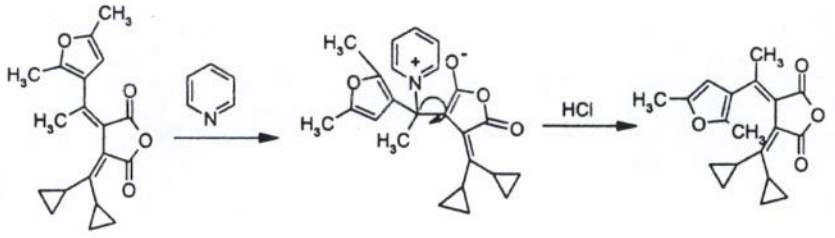
3-Z **3-E**

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

References

1. Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans. 2* **1981**, 341.
2. Heller, H. G. *IEE Proceedings* **1983**, *130*, 209.
3. Wittall, J. In *Photochromism, Molecules and Systems*; Durr, H.; Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990; p. 314.
4. Yokoyama, Y. *Chem. Rev.* **2000**, *100I*, 1717.
5. Hirshberg, Y.; Fischer, E. *J. Chem. Soc.* **1954**, 3129.
6. McArdle, C. B. In *Applied Photochromic Polymers*; McArdle, C. B., Ed.; Blackie: London, 1992; p. 1.