Highly Diastereoselective Photochromic Cyclization of a Bisthienylfulgide

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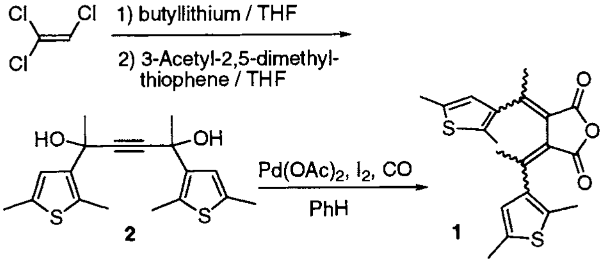
A fulgide, 3,4-bis[1-(2,5-dimethyl-3-thienyl)ethylidene]-3,4-dihydro-2,5-furandione, was synthesized by Pd-catalyzed carbonylation of the corresponding 2-butyne-1,4-diol derivative. UV-irradiation to the *ZZ*-form in toluene resulted in the formation of two diastereomeric colored forms by way of *EE*- and *EZ*-forms. The colored form from the *EE*-form was predominant in 90% de.

We have demonstrated that use of lithium diisopropylamide (LDA) and $CeCl_3$–LDA as base for Stobbe condensation to obtain sterically congested or electronically less reactive fulgides was effective.[1,2] Despite these improvements, highly crowded fulgides such as 3,4-bis[1-(2-alkyl-3-heteroaryl)ethylidene]-3,4-dihydro-2,5-furandione have not been synthesized so far.[1]

We have reported the synthesis and photochromism of some sterically demanding fulgides by Pd-catalyzed carbonylation of suitably substituted 2-butyne-1,4-diols.[3] We here report the synthesis of a highly congested, thermally irreversible fulgide **1** by the Pd-catalyzed carbonylation method, and the remarkable diastereoselectivity of photochromism of **1**.

Synthesis of **1** was done as follows (Scheme 1). Treatment of trichloroethene with 3 eq. of butyllithium followed by addition of 1 eq. of 3-acetyl-2,5-dimethylthiophene gave the acetylenediol **2** in 45% yield.[4] Reaction of **2** with carbon monoxide (8.1 MPa) in the presence of $Pd(OAc)_2$ and I_2 in benzene at 90 °C for 14 h afforded **1** as a mixture of geometric isomers, which were separated by silica gel flash column chromatography to give **1*EE***, **1*EZ***, and **1*ZZ*** in 4, 3, and 1% yields, respectively.[5] They were purified by recrystallization for photoreactions.



Scheme 1. Synthesis of **1**.

The identification of geometric isomers was done by ^1H NMR. Two isomers have symmetric structures because only three methyl signals and one aromatic proton signal were observed, whereas the other one showed six methyl signals and two aromatic proton signals. Therefore the last one was unequivocally assigned to **1*EZ***. One of the two symmetric isomers showed the signal of the proton on C(3) of thiophene at δ 5.98 whereas the other at 6.59. As the high-field shift of the former is best explained by the shielding effect of the aromatic ring, it is assigned to **1*EE***. Therefore the remaining one is assigned to be **1*ZZ***. The assignments were further confirmed by the photochemical behavior that **1*EE*** turned red much more quickly than **1*ZZ*** upon UV irradiation.

Photochromism of **1** was expected to occur between a set of isomers; i.e. three colorless forms (**1*EE***, **1*EZ***, **1*ZZ***) and two diastereomeric colored forms ($\mathbf{1C}_{EE}$, $\mathbf{1C}_{EZ}$) as shown in Scheme 2. Indeed, 366-nm light irradiation to the toluene solution of **1*ZZ*** (Figure 1) afforded **1*EZ***, **1*EE***, and two colored species. The major colored form changed to **1*EE*** upon 554-nm light irradiation. Since photochromism of fulgides is known to obey Woodward-Hoffmann rules,[6] the major colored form was assigned to $\mathbf{1C}_{EE}$.[5]

Analysis of change in concentration of the isomers during photoirradiation determined by HPLC according to the previously reported method[7] gave the quantum yields of photoreactions, which are summarized in Scheme 2, and their absorption spectral data are shown in Table 1.

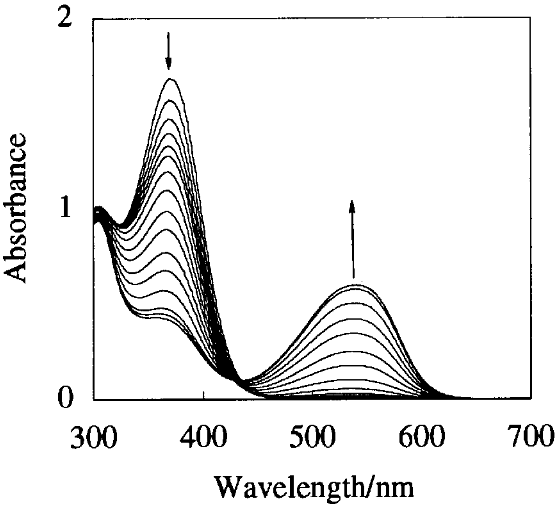
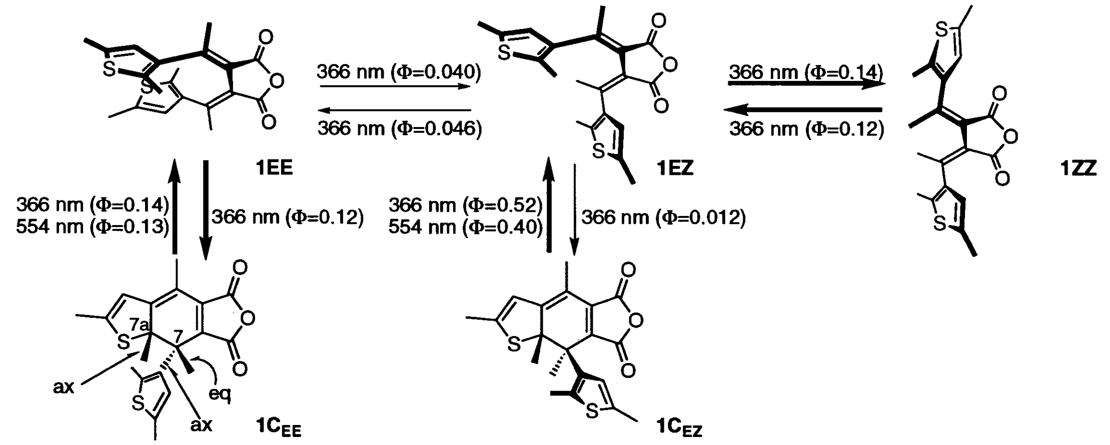


Figure 1. Spectral change of 366-nm light irradiation to **1ZZ** in toluene. c/mol dm^{-3}; 1.21 x 10^{-4}. Irradiation time/min; 0, 0.5, 1, 1.5, 2, 2.5, 3.5, 5, 7, 9, 12, 15, 20, 30, 40, 80.



Scheme 2. Photoreaction of **1**.

Table 1. Absorption spectral data of **1** in toluene

	1EE	1EZ	1ZZ	1C$_{EE}$	1C$_{EZ}$
λ_{max}/nm	362	362	372	541^a	532^a
ε_{max}/mol^{-1}dm^{3}cm^{-1}	6710	7670	13900	10200^a	7820^a

^{a}Calculated from the spectra of mixture of isomers with the known different concentrations.

At the photostationary state of UV-light irradiation, the ratio of concentration of the isomers, **1*EE***/**1*EZ***/**1*ZZ***/**1C**$_{EE}$/**1C**$_{EZ}$, was 17/14/8/58/3. The most notable feature is the highly diastereoselective formation of **1C**$_{EE}$ (90% de).[8] While the cyclization quantum yield of **1*EZ*** by 366-nm light irradiation ($\Phi_{EZ\text{-}C}$(UV)) is small, the reverse quantum yields ($\Phi_{C\text{-}EZ}$(UV)) and ($\Phi_{C\text{-}EZ}$(Vis)) are large. This is caused by the steric repulsion between the axial-like methyl group on C(7a) and the equatorial-like thiophene group on C(7) of **1C**$_{EZ}$. This was confirmed by PM3 molecular orbital calculations[9] that the rotation of the single bond between C(7) and the thiophene ring on C(7) of **1C**$_{EZ}$ is severely restricted. On the other hand, all the quantum yields between **1*EE*** and **1C**$_{EE}$ are large. This is due to the less steric repulsion between the substituents mentioned above, for both **1*EE*** and **1C**$_{EE}$. This time, the thiophene group on C(7) of **1C**$_{EE}$ is axial, and the rotation of the connecting single bond is not restricted.

The E-Z isomerization quantum yields by UV irradiation between **1*ZZ*** and **1*EZ*** are large. Because the geometry of at least one of the thienylethylidene groups is always *Z* for these two compounds, the steric repulsion is always small. However, isomerization from **1*EZ*** to **1*EE*** suffers a large increase in steric repulsion during the isomerization. Therefore the isomerization to **1*EE*** is the minor path. On the other hand, the major photochemical reaction of **1*EE*** is the cyclization rather than the E-Z isomerization. If an interaction like π-π stacking stabilization between the heteroaromatic rings would be working in **1*EE***, this result would be explained rationally.

In conclusion, (i) we have synthesized a thermally irreversible[10] photochromic fulgide **1** by Pd-catalyzed carbonylation method; (ii) This photochromic system showed the diastereoselective cyclization in which one of two diastereomeric colored forms is dominantly produced at the photostationary state.

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5 **1*EE***: ^{1}H NMR (CDCl$_3$, δ/ppm) 2.04 (6H, s), 2.27 (6H, s), 2.47 (6H, s), 5.98 (2H, s); IR (KBr, ν/cm^{-1}) 1807, 1759; mp 160 – 162 °C. **1*EZ***: ^{1}H NMR 1.46 (3H, s) 2.31 (3H, s) 2.36 (6H, s) 2.38 (3H, s) 2.67 (3H, s) 6.38 (1H, s) 6.49 (1H, s); IR 1811, 1763; mp 87 – 94 °C. **1*ZZ***: ^{1}H NMR 2.19 (6H, s) 2.36 (6H, s) 2.43 (6H, s) 6.59 (2H, s); IR 1823, 1767. mp *ca.* 200 °C (decomp). Satisfactory high resolution mass spectral data were obtained for above three compounds. **1C**$_{EE}$: ^{1}H NMR 1.61 (3H, s) 2.02 (3H, s) 2.17 (3H, s) 2.18 (3H, s) 2.25 (3H, s) 2.42 (3H, s) 6.03 (1H, s) 6.28 (1H, s).

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10 At 80 °C in toluene-d_8, change in the ratio of **1C**$_{EE}$ and **1*EE*** in a mixture of UV-irradiated sample was not observed by ^{1}H NMR for more than 100 h.