Pergamon

Tetrahedron Letters 40 (1999) 8067–8069

TETRAHEDRON
LETTERS

Synthesis of novel photochromic fluorescing 2-indolylfulgimides

Yongchao Liang, A. S. Dvornikov and P. M. Rentzepis *

Department of Chemistry, University of California, Irvine, CA 92697, USA

Received 26 July 1999; revised 7 September 1999; accepted 8 September 1999

Abstract

A series of novel *N*-substituted, thermally stable photochromic fluorescing 2-indolylfulmides were synthesized with high yields (>80%) from the corresponding fulgides by Lewis acid and hexamethyldisilazane-promoted one-pot reaction. © 1999 Elsevier Science Ltd. All rights reserved.

Photochromic materials have received much attention because of their potential application to rewriteable high capacity optical memories, optical switches, and high intensity light limiters.[1–3] Photochromic fulgides belong to one of the most important families of compounds which show excellent photochromic behavior, stability of both forms and reversibility making them potential materials for many electronic applications.[4,5]

The fulgimides, which are derivatives of fulgides, not only exhibit the excellent photochromic properties of their precursor fulgides, but in contrast to fulgides they are also chemically stable to acid or base-catalyzed hydrolysis.[6] An additionally important aspect of these fulgimides is that the *N*-substituent can be used as a linking group to prepare photochromic copolymers, photochromic liquid crystals, photoregulated binding of proteins, and photochromic Langmuir–Blodgett films.[7–9]

The fulgimides reported so far have been synthesized, to a large extent, by the condensation of fulgides and amines at high temperatures followed by the cyclization of the *N*-substituted amic acid in the presence of acidic reagents, such as acetic anhydride, or acetyl chloride.[10] However, low reaction yields have been reported for the conversion of succinamic acids, derivatized from fulgides with acid sensitive heterocyclic groups. These low yields limit the utilization of fulgimides in practical devices.[11]

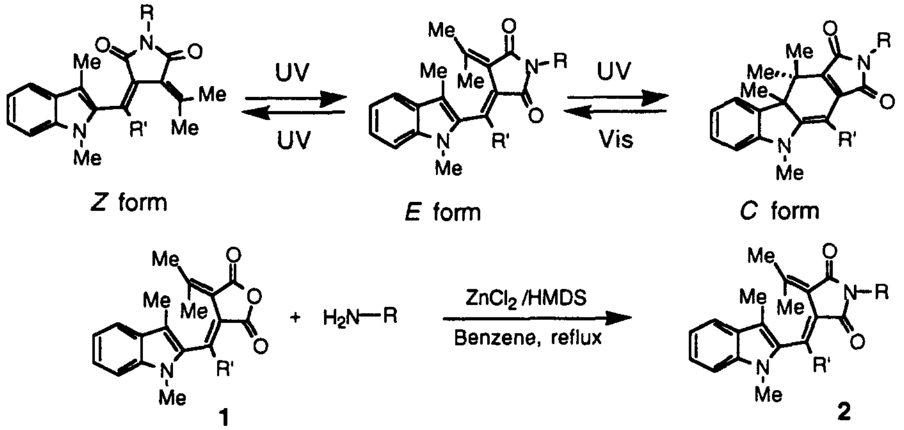
In this communication, we present our primary results on the synthesis of new photochromic fluorescent 2-indolylfulgimides using the simple and efficient method shown in Scheme 1, based upon the method of Toru for the synthesis of *N*-alkyl- and *N*-arylimide derivatives by Lewis acid and hexamethyldisilazane (HMDS)-promoted one-pot reaction.[12] The synthesized fulgimide molecules show excellent photochromic properties and the colored form fluoresces when irradiated with visible light.

The synthesis was performed as follows: Into a solution of fulgide **1a**[5] (0.233 g, 0.79 mmol) in benzene (12 mL), benzylamine (0.79 mmol) in benzene (5 mL) was added and stirred for 1 h at room temperature.

---

* Corresponding author.

PII: S0040-4039(99)01702-5



2a. R = $-CH_2C_6H_5$, R' = H, 4h, 93% ; **2b.** R = $-C_6H_5$, R' = H, 8h, 94%;

2c. R = $-CH_2CH{=}CH_2$, R' = H, 4h, 83%; **2d.** R = $-(CH_2)_3CH_3$, R' = H, 5h, 93%;

2e. R = $-C_6H_4CH{=}CH_2$, R' = H, 12h, 80%; **2f.** R = $-CH_2C_6H_5$, R' = CH_3, 5h, 95%

Scheme 1.

To this reaction mixture, zinc chloride (0.110 g, 0.79 mmol, commercial product, dried in a vacuum desiccator overnight) powder was added in one portion. Subsequently, the reaction mixture was heated to refluxing temperature (80°C), and a solution of hexamethyldisilazane (HMDS) (0.26 mL, 1.2 mmol) in benzene (5 mL) was added in 10 min intervals. This reaction mixture was then refluxed for 4 h and monitored by TLC. After removal of the solvent using a rotavapor, the crude product was purified by means of a flash silica gel chromatography column (chloroform as eluant) to afford a bright yellow solid **2a** (0.284 g, 93%).[13]

All fulgimides that were thus obtained exhibited excellent photochromic properties and thermal stability. Fig. 1 shows the UV–vis absorption spectra of **2a** in acetonitrile, in its *E* (colorless) and *C* (colored) forms and the fluorescence spectra emitted by the colored form in the same solvent. In contrast to the other previously investigated fulgimides,[11] the colored forms *C*, of fulgimides **2a**–**2f**, emitted fluorescence (see Fig. 1). To confirm, that the observed fluorescence is emitted by the colored forms of these fulgimides, rather than impurities or other species, we measured the excitation spectra and fluorescence emission spectra intensity change as a function of bleaching/coloration cycles. The data show that the fluorescence intensity and the excitation spectra of the colored form decreased proportionally with the bleaching of the fulgimides. When the solution was completely bleached, i.e. the absorption band of the *C* form disappeared, no fluorescence was detected. The fluorescence appeared again and increased at the same rate as the rate of the growth of the *C* form concentration. Fulgimide **2e** was found to have a quantum efficiency of 0.14 for ring-closing (coloration), 0.068 for ring-opening (bleaching) and 0.073 for fluorescence emission (colored form, excited at 550 nm). The method which was used for the measurement of the quantum efficiencies has been described previously.[14] All of these processes were measured in acetonitrile solution. These values are similar to the values of the corresponding fulgide.

In conclusion, we have successfully synthesized a series of novel photochromic fluorescent 2-indolylfulgimides by means of the simple and efficient Lewis acid and hexamethyldisilazane-promoted one-pot reaction with high yield (more than 80%). This method may also be used for the transformation of a wide range of other heterocyclic fulgides to their corresponding fulgimides.

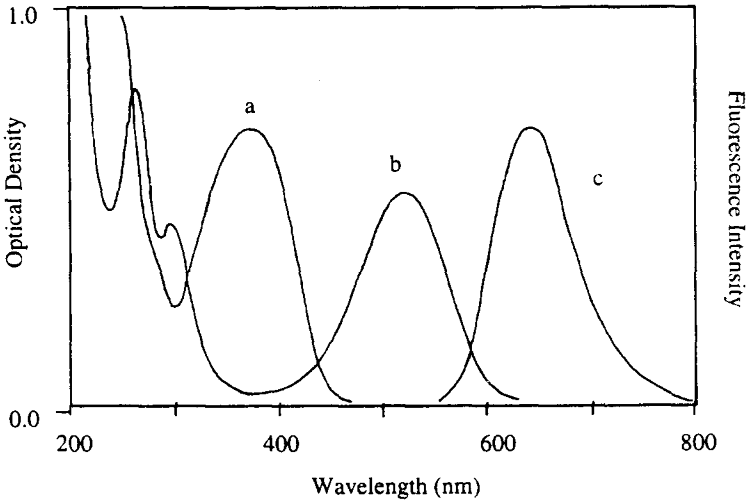


Figure 1. Absorption and fluorescence spectra of fulgimide **2a**. (a) Absorption spectrum of *E* form; (b and c) absorption and fluorescence spectra of *C* form; all in acetonitrile solution

Acknowledgements

This work was partly supported by the United States Air Force, Rome Laboratory, under contract number F 30602-97-C-0029.

References

1. Proceedings of the Second International Symposium on Photochromism, Florida, USA, September, 1996, *Molecular Crystals and Liquid Crystals*, 1997, Vol. 297–298.
2. Durr, H.; Bouas-Laurent, H. *Photochromism. Molecules and Systems*; Elsevier: Amsterdam, 1990.
3. Dvornikov, A. S.; Cokgor, I.; Wang, M.; McCormick, F. B.; Esener, S. E.; Rentzepis, P. M. *IEEE CPMT A*, **1997**, *20*, 203.
4. Heller, H. G. *CRC Handbook of Organic Photochemistry and Photobiology*; CRC Press, 1995; pp. 174.
5. Liang, Y. C.; Dvornikov, A. S.; Rentzepis, P. M. *Res. Chem. Intermed.* **1998**, *24*, 905.
6. Matsushima, R.; Sakaguchi, H. *J. Photochem. Photobio. A: Chem.* **1997**, *108*, 239.
7. Willner, I.; Rubin, S.; Wonner, J.; Effenberger, F.; Bauerle, P. *J. Am. Chem. Soc.* **1992**, *114*, 3150.
8. Cabrera, I.; Dittrich, A.; Ringsdorf, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 76.
9. Deblauwe, V.; Smets, G. *Macromol. Chem.* **1988**, *189*, 2503.
10. Hart, R. J.; Heller, H. J. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1321.
11. Heller, H. G.; Koh, K.; Elliot, C.; Whittall, J. *J. Mol. Cryst. Liq. Cryst.* **1994**, *246*, 79.
12. Reddy, P. Y.; Kondo, S.; Toru, T.; Ueno, Y. J. *J. Org. Chem.* **1997**, *62*, 2652.
13. Mp: 178.5–179.5°C, ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ: 1.25 (s, 3H), 1.94 (s, 3H), 2.47 (s, 3H), 3.70 (s, 3H), 4.83 (s, 2H), 7.10–7.65 (m, 10H); ^{13}C NMR (500 MHz, $CDCl_3$, TMS) δ: 10.6, 22.6, 26.9, 30.8, 41.8, 109.1, 115.1, 119.5, 121.2, 122.4, 123.5, 127.1, 127.6, 127.7, 128.4, 128.6, 132.8, 136.5, 138.4, 153.5, 168.3, 168.9; HRMS (CI) *m/z* calcd for $C_{25}H_{24}N_2O_2$: 384.1838 (M^+). Found: 384.1833; Anal. calcd for $C_{25}H_{24}N_2O_2$: C, 78.09; H, 6.30; N, 7.29. Found: C, 77.37; H, 6.26; N, 7.18.; spectra data of other compounds will be published elsewhere.
14. Liang, Y. C.; Dvornikov, A. S.; Rentzepis, P. M. *J. Photochem. and Photobiol. A: Chem.* **1999**, *125*, 79.