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Short note

Microwave-assisted synthesis of photochromic fulgimides

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Abstract

A series of photochromic fulgimides have been successfully synthesized from their respective fulgides using microwave methodology. The yields of the fulgimides synthesized through this method, were an improvement over the thermal methods usually employed.

Keywords: Photochromic; Fulgides; Fulgimides; Microwave; Synthesis

1. Introduction

Photochromic fulgides [1a,b] have been extensively studied and synthesized by many groups around the world. To be photochromic, fulgides should have at least one aromatic ring on the exo-methylene carbon atom, so that they form a 1,3,5-hexatriene structure that may undergo 6π-electrocyclization [2a–c]. One significant property of aromatic heterocyclic fulgides is the thermal stability of their open- or closed-form. In addition, good separation of absorption spectra of both forms also enable these fulgides to be considered for potential application in optical memory devices and optical switches [1,3].

To date, a wide range of fulgides with aromatic heterocycles have been synthesized and fully characterized [2a,4a–d]. Furthermore, molecular tailoring of these fulgides have been also extensively carried out by several groups, Heller, Rentzepis and co-workers, and Matsushima et al., to name a few [5a–c]. To be able to achieve certain desirable properties, the fulgide anhydride core has been subjected to various modifications and has also been reported extensively [6a–d].

In our laboratory, fulgides **1** [2] and **2** [7] were synthesized according to literature procedures with yields of 45 and 55%, respectively (Scheme 1). These fulgides were further reacted with selected amines to afford their corresponding fulgimides. Fulgimides are usually less colored than their corresponding fulgides, but show similar photochromic properties [1b,8]. Fulgimides have been known to be more resistant to acid- or base-catalyzed hydrolysis than their corresponding fulgides, but their resistance to photodegradation is not markedly improved [9]. The importance of fulgimides is that the N-substituent can be used as a linking group to prepare photochromic Langmuir–Blodgett films [10], photochromic liquid crystals [11], photochromic diagnostic devices [12], and photochromic copolymers [13]. Fulgimides are usually synthesized using the methodology developed by Heller [14]. In our laboratory, attempts at refluxing acetyl chloride for the generation of the fuligmide resulted in many decomposed products and low yields of desired fulgimides. As such, we decided to search for milder methods.

We explored the possibility of using microwave technology, in order to develop an efficient and fast method of obtaining fulgimides in a mild fashion. Many papers and reviews have been published in recent years concerning microwaves in organic chemistry [15a–f]. The relatively low cost of modem domestic microwave ovens makes them reasonably readily available to academic and industrial chemists; however, somewhat surprisingly only a relatively small number of organic synthesis research groups have reported their use [16a–c].

2. Results and discussion

With reference to the synthesis of phthalimides using microwave as reported by Bogdal et al. [17a,b] Chandrasekhar et al. [18] and Borah et al. [19] we decided to investigate if we could

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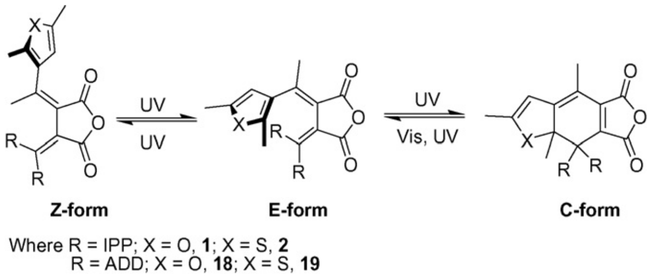
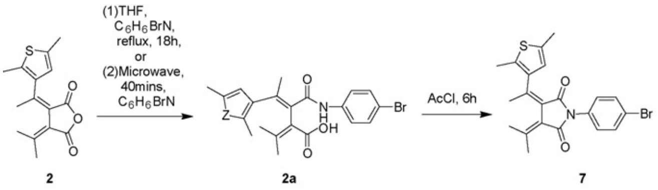


Scheme 1.



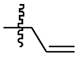
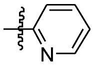
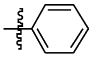
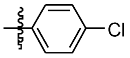
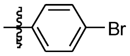
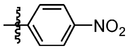
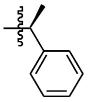
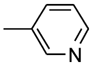
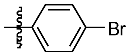
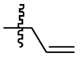
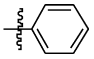
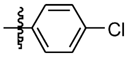
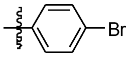
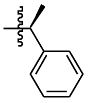
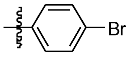
(1) Classical fulgimide synthesis - total synthesis time: ~24h; Yield of **7**, 40%
(2) Microwave-assisted fulgimide synthesis - total synthesis time: <7h; Yield of **7**, 73%

Scheme 2.

also use microwave irradiation for the formation of the desired amide, as an alternative to the harsh conditions mentioned. We first started an initial synthesis of fulgimide **7** (Scheme 2.) in an effort to improve the yield of the molecule using milder conditions. Surprisingly, the reaction to form the half-amide **2a**, from **2**, took no longer than 40 min, with the subsequent ring closure, employing an excess of acetyl chloride, stirring at room temperature for 4–6 h afforded fulgimide **7** with yields of up to 73% [20]. This improvement in yield from the thermal heating route to obtain **7** was almost 2-fold and the reaction time was reduced by almost 3-fold [21]. We also employed the classical fulgimide synthetic route towards fulgimides **3–17** as a comparison between the microwave methodology and the thermal heating methodology. Thermal heating was carried out for only the formation of the amide and stirring at room temperature was carried out for the ring-closure step.

Based on the successful result obtained from the microwave reaction, we decided to screen through a series of amines, to determine if we could also synthesize other less accessible fulgimides, based on our synthetic study. Using the microwave-assisted strategy, we managed to successfully synthesize a series of fulgimides with yields up to 85%. With reference to Table 1,

Table 1
Improved yields of thienyl-fulgimides obtained through microwave-assisted synthesis

	R^2NH_2	R^1 (IPP/ADD)	Z (S/O)	Microwave power	Time (min)	$ZnCl_2$ method yield (%)	Thermal heating yield (%)	Microwave yield (%)
3		IPP	S	High	40	–	5–42	47
4		IPP	S	High	40	0–15	20–39	16
5		IPP	S	High	40	–	42	65
6		IPP	S	High	40	40	65	85
7		IPP	S	High	40	–	40	73
8		IPP	S	High	35	–	0	36
9		IPP	S	High	25	–	6–70	74
10		IPP	S	High	40	–	0	2
11		ADD	S	High	40	0	0	60
12		IPP	O	High	40	–	35	42
13		IPP	O	High	25	–	39	57
14		IPP	O	High	40	–	60	70
15		IPP	O	High	40	–	52	65
16		IPP	O	High	25	–	65	69
17		ADD	O	High	40	–	0	75

we observed that the microwave-assisted synthesis of fulgimides generally lead to a yield improvement when compared with the other methods tried. For fulgimide **3**, the yield obtained was almost identical to the traditional method of refluxing the fulgide with the amine. However, the more significant difference with the two reactions would be the faster reaction time and minimal use of organic solvent. We managed to obtain fulgimide **5** with a yield of 65%. This was generally an improvement of 23% over the classical approach. Activated amines generally gave higher yields when we used the microwave approach [22]. Theinyl-fulgimides **5**, **6** and **7** were obtained with improved yields of up to 85%. Fulgimide **9** was also obtained with a respectable yield of 74%. However, fulgimides **4** and **10** were obtained in very low yields probably due the unreactive electron-poor amino-pyridines employed.

Riding on the success of the ability to effect functionalization, we decided to use 4-bromo-aniline to form the brominated fulgimide derivatives of ADD fulgides **18** and **19** [23]. This was to allow us to further extend the chemistry of the fulgimides through a possible Heck reaction with other potential substrates. Accordingly, we were able to obtain satisfactory yields of 60% for fulgimide **11** and 75% for fulgimide **17**. We also employed furyl-fulgides **1** and **18**, to synthesize the corresponding fulgimides, **12–17**. Yields obtained were comparable to the thienyl-fulgimides **3–11**. Comparatively, the thermal heating route afforded yields lower by up to 18%.

3. Conclusion

As a conclusion, a series of fulgimides were synthesized successfully with improved yields over thermal methods employing microwave. This methodology also reduced the reaction time and organic solvents used. A commercially available microwave synthesizer would provide an avenue towards optimization of the reaction conditions.

Full supporting information of all synthesized molecules is available.

Acknowledgment

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2006.05.018.

References

[1] (a) J. Whittall, in: H. Dürr, H. Bouas-Laurent (Eds.), Photochromism: Molecules and Systems, Elsevier, Amsterdam, 1990, pp. 467–492;
(b) Y. Yokoyama, Chem. Rev. 100 (2000) 1717–1739.

[2] (a) H.G. Heller, S. Oliver, J. Chem. Soc. Perkin Trans. 1 (1981) 197–201;
(b) P.J. Darcy, H.G. Heller, P.J. Strydom, J. Whittall, J. Chem. Soc. Perkin Trans. 1 (1981) 202–205;
(c) H.G. Heller, J.R. Langan, J. Chem. Soc. Perkin Trans. 2 (1981) 341.

[3] J.C. Crano, R.J. Guglielmetti, Organic Photochromic and Thermochromic Compounds, Kluwer Academic Publishers, New York, 1999.

[4] (a) A. Kaneko, A. Tomoda, M. Ishizuka, H. Suzuki, R. Matsushima, Bull. Chem. Soc. Jpn. 61 (1988) 3569;
(b) L. Yu, Y. Ming, W. Zhao, M. Fan, J. Photochem. Photobiol. A Chem. 68 (1992) 309;
(c) Y. Yokoyama, Y. Kurita, Mol. Cryst. Liq. Cryst. Sect. A 246 (1994) 87;
(d) J. Walz, K. Ulrich, H. Port, H.C. Wolf, J. Wonner, F. Effenberger, Chem. Phys. Lett. 213 (1993) 321–324.

[5] (a) H.G. Heller, Fulgimide derivatives. Brit. 1972. 7. CODEN: BRXXAA GB 1271655 19720426 CAN 77:61806 AN 1972:461806;
(b) Y. Liang, A.S. Dvornikov, P.M. Rentzepis, Macromolecules 35 (25) (2002) 9377–9382;
(c) R. Matsushima, H. Sakaguchi, J. Photochem. Photobiol. A 108 (1997) 239.

[6] (a) H.G. Heller, D.S. Hughes, M.B. Hursthouse, N.G. Rowles, Chem. Commun. (2000) 1397;
(b) Z. Sun, R.S. Hosmane, J. Heterocycl. Chem. 32 (1995) 1819;
(c) Y. Yokoyama, K. Takahashi, Chem. Lett. (1996) 1037;
(d) I. Cabrera, A. Dittrich, H. Ringsdorf, Angew. Chem. Int. Engl. 30 (1991) 76.

[7] A.P. Glaze, S.A. Harris, H.G. Heller, W. Johncock, S.N. Oliver, P.J. Strydom, J. Whittall, J. Chem. Soc. Perkin Trans. 1 (5) (1985) 957–961.

[8] Where IPP = isopropylidene and ADD = adamantylidene.

[9] M.A. Wolak, C.J. Thomas, N.B. Gillespie, R.R. Birge, W.J. Lees, J. Org. Chem. 68 (2) (2003) 319–326.

[10] I. Cabrera, D. Achim, H. Ringsdorf, D.E. 4007636A1.

[11] I. Cabrera, D. Achim, H. Ringsdorf, Angew. Chem. Int. Ed. 30 (1991) 76.

[12] I. Willmer, S. Rubin, J. Wonner, F. Effenberger, P. Bauerle, J. Am. Chem. Soc. 114 (1992) 3150.

[13] C.C. Elliot, M.Sc. Thesis; University of Wales, Cardiff, 1990.

[14] H.G. Heller, Fulgimide derivatives. Brit. 1972. 7. CODEN: BRXXAA GB 1271655 19720426 CAN 77:61806 AN 1972:461806.

[15] (a) R.A. Abramovitch, Org. Prep. Proc. Int. 23 (1991) 683–711;
(b) A.G. Whittaker, D.M.P.J. Mingos, Microwave Power Electromangetic Energy 29 (1994) 195–219;
(c) D.M.P. Mingos, Res. Chem. Intermed. 20 (1994) 85–91;
(d) D.M.P. Mingos, D.R. Baghurst, Chem. Soc. Rev. 20 (1991) 1–47;
(e) G. Majetich, R. Hicks, Radiat. Phys. Chem. 45 (1995) 567–579;
(f) S. Caddick, Tetrahedron 51 (1995) 10403–10432.

[16] (a) R. Gedye, F. Smith, K. Westaway, Educ. Chem. (1988) 55;
(b) M. Ali, S.P. Bond, S.A. Mbogo, W.R. McWhinnie, P.M.J. Watts, Organomet. Chem. 11 (1989) 371;
(c) A.K. Bose, M.S. Manhas, M. Ghosh, V.S. Raju, K. Tabei, Z. Urbanezyk-Lipkowska, Heterocycles 30 (1990) 741.

[17] (a) D. Bogdal, J. Pielichowski, A. Boron, Synlett (1996) 873;
(b) D. Bogdal, J. Pielichowski, K. Jaskot, Heterocycles 45 (1997) 715.

[18] S. Chandrasekhar, M. Takhi, G. Uma, Tetrahedron Lett. 38 (1997) 8089.

[19] H.N. Borah, R.C. Boruah, J.S. Sandhu, J. Chem. Res. 8 (1998) 272.

[20] Representative experimental procedure: To a round bottomed flask (RBF) containing the fulgide and the selected amine, was added 2 ml of THF. The mixture was allowed to dissolve and was mixed well before being subjected to microwave radiation. The reaction was carried out without a stopper or plug so as to allow the evaporation of solvent and prevent a build-up of pressure in the reaction vessel. After the stated time, the RBF was removed and the crude reaction mixture treated with acetyl chloride for up to 6 h. This was followed by removal of excess acetyl chloride and volatiles via vacuo, before subjecting the crude mixture to flash chromatography. Supporting information for fulgimide **11**: Z-form: 1H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, 2H), 7.25 (d, 2H), 6.51 (s, 1H), 4.54 (s, 1H), 2.73 (s, 1H), 2.39 (s, 3H), 2.30 (s, 3H), 2.15 (s, 3H), 2.06–1.93 (m, 12H) ppm. 13C NMR (300 MHz, $CDCl_3$) δ 167.2, 166.8, 164.4, 142.6, 136.3, 135.6, 131.7, 131.2, 128.4, 124.6, 121.4, 117.2, 39.6, 37.7, 36.5, 32.8, 27.4, 26.2, 15.2, 14.2 ppm. FTIR (KBr): 3441, 2936, 2916, 2899, 2850, 1753, 1710, 1620, 1487, 1361, 1129, 821, 778, 756, 504 cm^{-1}. UV(vis) Z-form: O: 340 nm,

C: 574 nm. HRMS (EI) Calculated for $C_{28}H_{28}BrNO_2S$ [M^+]: 521.1024, found: 521.1020; [M^+-CH3]: 506.0789, found: 506.0819.

[21] We extended the heating time for the synthesis of the half-amide as the reaction was not completed even after 2–4 h of heating as reported in literature. It was only after refluxing the mixture overnight or up to 24 h were we able to obtain almost complete disappearance of the starting material. Thin layer chromatography (TLC) monitoring was used throughout the reaction. Please refer to supporting information pages S4 and S5 for more experimental details.

[22] Microwave reactions were carried out in duplicate in order to ascertain the reproducibility of the reaction. Scale up (5 mmol) of the reaction towards fulgimide **17** also gave yields up to 70%. The microwave oven used was a conventional microwave oven operating with a power range of 1000–1200 W. This is the highest setting for the microwave oven. Although the power cannot be controlled accurately, the timing of the reaction can be controlled using a stop watch and by switching the microwave oven on or off accordingly.

[23] ADD Fulgides **18** and **19** were obtained with 41% and 54%, respectively.