Arabian Journal of Chemistry (2014) 7, 972–975

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

A novel method for the synthesis of coumarin laser dyes derived from 3-(1H-benzoimidazol-2-yl) coumarin-2-one under microwave irradiation

Ghasem Bakhtiari [a,b,*], **Shahram Moradi** [a], **Saeed Soltanali** [c]

[a] *Faculty of Science, Islamic Azad University (Tehran North Branch), Tehran, Iran*
[b] *Chemistry Departments, Amirkabir University of Technology, P.O. Box 15875-4413, Tehran, Iran*
[c] *Chemical Engineering Departments, Amirkabir University of Technology, P.O. Box 15875-4413, Tehran, Iran*

Received 27 October 2010; accepted 11 December 2010
Available online 5 January 2011

KEYWORDS

Dye;
Coumarin;
Microwave;
Synthesis

Abstract We want to achieve the synthesis of 3-(1*H*-benzoimidazol-2-yl)-7-(diethylamino) coumarin-2-one (**1**), 3-(1*H*-benzoimidazol-2-yl)-7-(dimethylamino) coumarin-2-one (**2**), 3-(1*H*-benzoimidazol-2-yl) coumarin-2-one (**3**) that are important dyes in industries (Soko owska et al., 2001). Methods for the synthesis of some of these compounds have been the title in some pervious patents, but enough information about separation and purification of them was not clearly indicated. We carried out several methods for the synthesis of the mentioned compound and purification with different yields. Now, we can synthesise these dyes under microwave irradiation in solid phase and solvent free methods with 80% yield, which is a high and remarkable percentage.

1. Introduction

Coumarin is an oxygen heterocycle. Coumarin compounds find widespread usage in many applications; several fluorescent organic chromophores derived from coumarin have been used as fluorescent brighteners, laser dyes and organic nonlinear optical materials (Fischer and Cremer, 1995; Soko owska et al., 2001; Zhao et al., 1982). Coumarins seem to work as pesticides in the plants that produce them. Coumarins are responsible for the sweet smell of new mown hays. Coumarins constitute the largest class of laser dyes in the 'blue-green' region (Drexhage, 1976; Holman et al., 1984). Due to their inherent photochemical characteristics, reasonable stability, good solubility and relative ease of synthesis coumarin derivatives have been extensively investigated for electronic and photonic applications, such as charge-transfer agents, solar energy collectors and nonlinear optical materials (Ayyangar et al., 1991, 1995).

Coumarins are widely used as fluorescent labels and pigments (Schwander et al., 1988), as fluorescent probes for physiological (Christie, 1993) and enzymatic measurements, as signaling units in sensors (Alonso et al., 2002; Leray et al.,

* Corresponding author at: Faculty of Science, Islamic Azad University (Tehran North Branch), Tehran, Iran.Tel.: +98 21 48253206, fax: +98 21 48259738.
E-mail address: bakhtiarigh@ripi.ir (G. Bakhtiari).
Peer review under responsibility of King Saud University.

ELSEVIER Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.arabjc.2010.12.012

2000) in markers and in sophisticated photo physical systems (Duarte et al., 2006; Li et al., 2006). Coumarin chromophores exhibit intense fluorescence on the substitution of various functional groups at different positions (Eggeling et al., 2002) and appropriately substituted coumarins find application as fluorescent dyes for synthetic fibers and as daylight fluorescent pigments, which impart bright brilliance to paints and printing inks (Ward and Kimmel, 1982). It is well known that the property of fluorescence in the coumarin chromophore system is significantly altered by an appropriate substituent at the 3- and the 7-positions. Electron donors, such as amino, hydroxyl and methoxy groups at the 7-position and electron acceptor heterocyclic rings, such as benzothiazole, benzoxazole and benzimidazole at the 3-position impart distinct bathochromicity and strong fluorescence. Most of the coumarin based chromophores reported in the literature absorb in the range of 420–450 nm. In this communication, microwave heating has taken an incontrovertible place in analytical and organic laboratories' practice as a very effective and non-polluting method of activation. The main purpose for this increase include the availability of commercial microwave equipment devoted for organic chemistry and the development of solvent free methods, which have improved the safety aspects, but are mostly due to an increased interest in shorter reaction times. There are many examples of this technology in digestion and organic synthesis. (Abramovitch, 1991; Loupy, 1993; Majetich and Hicks, 1994; Strauss and Trainor, 1995; Deshayes et al., 1999; De la Hoz et al., 2000; Lidström et al., 2001; Lew et al., 2002).

We report the synthesis of 3-(1*H*-benzoimidazol-2-yl)-7-(diethylamino) coumarin-2-one (**1**) and 3-(1*H*-benzoimidazol-2-yl)-7-(dimethylamino) coumarin-2-one (**2**) and 3-(1*H*-benzoimidazol-2-yl) coumarin-2-one (**3**) with solvent and without solvent by microwave (green chemistry). The most popular and cheap equipment in organic synthesis is the domestic oven (with limited power at 800–1000 W).

These three compounds are categorized as important florescent dyes. These coumarin compounds are widely used in laser industry as laser dyes and some of them have been titled in some previous patents without an explanation of how they have been synthesised and besides we offer a new method for their synthesis by means of microwave irradiation.

2. Experimental

*2.1. Synthesis of 3-(1**H**-benzoimidazol-2-yl)-7-(diethylamino) coumarin-2-one (**1**) and 3-(1**H**-benzoimidazol-2-yl)-7-(dimethylamino) coumarin-2-one (**2**) and 3-(1**H**-benzoimidazol-2-yl) coumarin-2-one (**3**) (the solvent method)*

*2.1.1. Synthesis of 3-(1**H**-benzoimidazol-2-yl)-7-(diethylamino) coumarin-2-one (**1**)*

7-(Diethylamino)-2-oxo-2*H* coumarin-3-carboxilic acid (3.2 g) and *o*-phenylenediamine (0.8 g) were dissolved in H_2SO_4 50% (30 g). The mixture was refluxed for 8 h and was filtered out, dried and individuated by TLC in silica gel column, eluent for **1** (*n*-hexane–AcOEt 3:7). Yield 2.1 g (52%) of yellow solid, mp 210–211 °C (Hausermann and Valtz, 1967, 1961).

7-(Diethylamino)-2-oxo-2*H* coumarin-3-carboxilic acid (3.2 g) and *o*-phenylenediamine (0.8 g) were dissolved in ethanol (15 mL). The mixture was refluxed for 8 h and was filtered out and dried and individuation by TLC in silica gel column, eluent for **1** (*n*-hexane–AcOEt 3:7). Yield 2.0 g (50%) of yellow solid, mp 210–211 °C.

7-(Diethylamino)-2-oxo-2*H* coumarin-3-carboxilic acid (3.2 g) and *o*-phenylenediamine (0.8 g) were dissolved in toluene (15 mL). The mixture was refluxed for 18 h and was filtered out and dried and individuation by TLC in silica gel column, eluent for **1** (*n*-hexane–AcOEt 3:7). Yield 2.0 g (50%) of yellow solid, mp 210–211 °C.

*2.1.2. Synthesis of 3-(1H-benzoimidazol-2-yl)-7-(dimethylamino) coumarin-2-one (**2**)*

7-(Dimethylamino)-2-oxo-2*H* coumarin-3-carboxilic acid (3.2 g) and *o*-phenylenediamine (0.8 g) were dissolved in toluene (15 mL). The mixture was refluxed for 18 h and was filtered out and dried and individuation by TLC in silica gel column, eluent for **2** (*n*-hexane–AcOEt 3:7). Yield 2.0 g (50%) of yellow solid, mp 208–209 °C.

*2.1.3. Synthesis of 3-(1H-benzoimidazol-2-yl) coumarin-2-one (**3**)*

2-Oxo-2*H* coumarin-3-carboxilic acid (3.2 g) and *o*-phenylenediamine (0.8 g) were dissolved in toluene (15 mL). The mixture was refluxed for 18 h and was filtered out and dried and individuation by TLC in silica gel column, eluent for **3** (*n*-hexane–AcOEt 3:7). Yield 2.2 g (55%) of yellow solid, mp 206–207 °C.

*2.2. Synthesis of 3-1H-benzoimidazol-2-yl)-7-(diethylamino) coumarin-2-one (**1**) and 3-1H-benzoimidazol-2-yl)-7(dimethylamino) coumarin-2-one (**2**) and 3-(1H-benzoimidazol-2-yl) coumarin-2-one (**3**) (the microwave-assisted method)*

A mixture of amounts of **1**, **2**, **3** and *o*-phenylenediamine were exposed to MW irradiation (720 W) for about 6 min.

*2.2.1. Synthesis of 3-1H-benzoimidazol-2-yl)-7-(diethylamino) coumarin-2-one (**1**)*

7-(Diethylamino)-2-oxo-2*H* coumarin-3-carboxilic acid (1.16 g) and *o*-phenylenediamine (0.4 g) in the microwave oven (900 W) with 80% power for 355 s. Monitored by TLC on silica gel plates, eluent for **1** (*n*-hexane–AcOEt 3:7).

3-(1*H*-Benzoimidazol-2-yl)-7-(diethylamino) coumarin-2-one (**1**): Yield 1.23 g (80%) of yellow solid. The analytical sample was crystallized from 20 mL ethanol and recrystallized from 7 mL ethanol, mp 210–211 °C.

^{1}H NMR ($CDCl_3$, 300 MHz) 3-(1*H*-benzoimidazol-2-yl)-7-(diethylamino) coumarin-2-one (according to Fig. 1): δ 13.46 ppm, s br, 1H, (NH) δ 8.43 ppm, s, 1H, δ 7.21 ppm, d, 1H, J = 8.68 Hz, δ 7.05 ppm, d, 1H, δ 6.81 ppm, dd, 1H, δ 6.29 ppm, d, 1H, δ 6.22 ppm, d, 1H, δ 4.11 ppm, s br, 1H, (NH) δ 3.41 ppm, q, 4H, 2(CH_2), J = 7.12 Hz, δ 1.23 ppm, t, 6H, 2(CH_3), J = 7 Hz.

*2.2.2. Synthesis of 3-1H-benzoimidazol-2-yl)-7(dimethylamino) coumarin-2-one (**2**)*

7-(Dimethylamino)-2-oxo-2*H* coumarin-3-carboxilic acid (4 g) and *o*-phenylenediamine (1.38 g) in the microwave oven

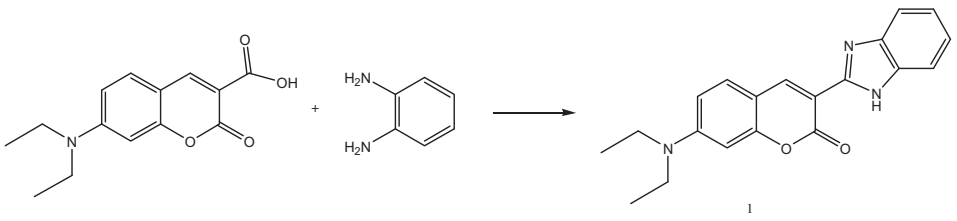

Figure 1 Structures of synthesized dye **1**.

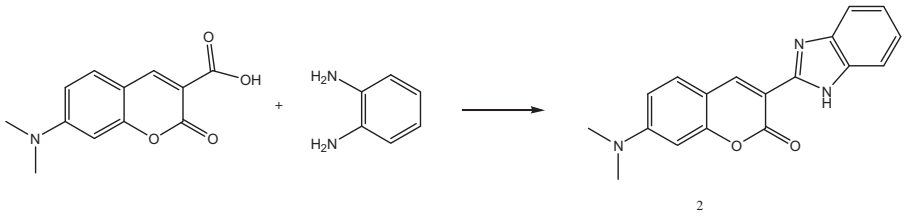

Figure 2 Structures of synthesized dye **2**.

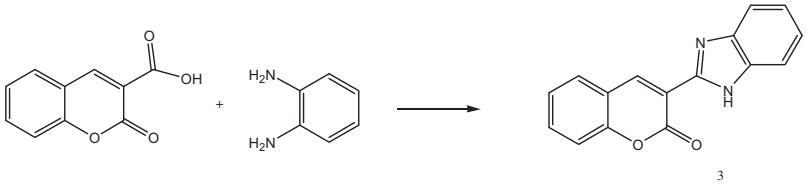

Figure 3 Structures of synthesized dye **3**.

(900 W) with 80% power for 360 s, monitored by TLC on silica gel plates, eluent for **2** (*n*-hexane–AcOEt 3:7).

3-(1*H*-Benzoimidazol-2-yl)-7-(dimethylamino) coumarin-2-one (**2**): Yield 4.46 g (83%) of yellow solid. The analytical sample was crystallized from 40 mL ethanol and recrystallized from 15 mL ethanol, mp 208–209 °C.

^{1}H NMR ($CDCl_3$, 300 MHz) 3-(1*H*-benzoimidazol-2-yl)-7-(dimethylamino) coumarin-2-one (according to Fig. 2): δ 13.46 ppm, s br, 1H, (NH) δ 8.43 ppm, s, 1H, δ 7.21 ppm, d, 1H, J = 8.68 Hz, δ 7.05 ppm, d, 1H, δ 6.81 ppm, dd, 1H, δ 6.29 ppm, d, 1H, δ 6.22 ppm, d, 1H, δ 4.11 ppm, s br, 1H, (NH), δ 3.5 ppm, S, 6H, ($2CH_3$).

*2.2.3. Synthesis of 3-(1H-benzoimidazol-2-yl) coumarin-2-one (**3**)*

2-Oxo-2*H* coumarin-3-carboxilic acid (4 g) and *o*-phenylenediamine (1.38 g) in the microwave oven (900 W) with 80% power for 370 s. Monitored by TLC on silica gel plates, eluent for **3** (*n*-hexane–AcOEt 3:7).

3-(1*H*-benzoimidazol-2-yl) coumarin-2-one (**3**): Yield 4.40 g (81%) of yellow solid. The analytical sample was crystallized from 40 mL ethanol and recrystallized from 15 mL ethanol, mp 206–207 °C.

^{1}H NMR ($CDCl_3$, 300 MHz) 3-(1*H*-benzoimidazol-2-yl) coumarin-2-one (according to Fig. 3): δ 12.3 ppm, s br, 1H, (NH) δ 8.1 ppm, s, 1H, δ 7.86 ppm, d., 1H, δ 7.47 ppm, d, 1H, δ 7.43 ppm, dd, 1H, δ 7.41 ppm, dd, 1H, δ 6.88 ppm, dd, 1H, δ 5.87 ppm, dd, 1H.

Table 1 Information of reaction for compounds.

No.	Compound number	Reaction condition	Solvent	Reaction time	Yield (%)
1	**1**	Solvent	H_2SO_4	8 h	52
2	**1**	Solvent	Ethanol	8 h	50
3	**1**	Solvent	Toluene	18 h	50
4	**2**	Solvent	Toluene	18 h	50
5	**3**	Solvent	Toluene	18 h	55
6	**1**	Solvent free	–	355 s	80
7	**2**	Solvent free	–	360 s	83
8	**3**	Solvent free	–	370 s	81

3. Chemicals and instruments

All chemicals were purchased from a major chemical supplier as high or highest purity grade and used without further purification from Aldrich Company. Prefabricated silica gel sheets (Merck Kieselgel 60 F254) were used for TLC. Melting points were determined with a Digital Melting Point Apparatus 9001 and are uncorrected. Microwave oven Plazmatronika 900 W (www.plazmatronika.pl), equipped with a single mode cavity suitable for the micro scale synthesis set to 80% power was used. ^{1}H NMR, spectra in solution were recorded at 25 °C with a Varian NMRS-300, and standard Varian software was employed Table 1.

4. Results and discussion

Dyes in this study were synthesized by different methods. Some of them (e.g., dye I) were previously presented as patents (Ohkawa and Ishii, 1967). Different evaluated methods, including solvent free method and solvent methods have been carried out.

In the solvent method, several solvents were used. In solvent method with ethanol, reaction time lasted about 8 h and it was a difficult process of separation and with 50% yield. Using toluene as a solvent was a time consuming process, in which reflux time lasted about 18 h, so it was difficult to take care; in addition the product was oily and its purification and isolation were hard and also with 50% yield. In the solvent method with Sulfuric acid, we had about 60% yields. Although there was a 10% increase of the product, reaction time was very long, and separation process was difficult to handle. One reason to this was acidity of the reflux product.

In the solvent method, no solvents are used and there are some noticeable advantages of using solvent free method. It is extremely safe, new with high efficiency (about 85%); furthermore it was a low cost process with a great speed in reaction and easy in separation and purification. There is another point to explain this method and it is too important to be ignored and it is "green chemistry" that is carefully regarded. In fact, solvent free method does agree with the environment and never creates pollution.

References

Abramovitch, R.A., 1991. Org. Prep. Proced. Int. 23, 685.

Alonso, M.T., Brunet, E., Juanes, O., Rodriguez-Ubis, J.C., 2002. J. Photochem. Photobiol. 147, 25.

Ayyangar, N.R., Srinivasan, K.V., Daniel, T., 1991. Dyes Pigm. 16, 197.

Christie, R.M., 1993. Rev. Prog. Color 23, 18.

De la Hoz, A., Diaz-Ortis, A., Moreno, A., Langa, F., 2000. Eur. J. Org. Chem., 3659.

Deshayes, S., Liagre, M., Loupy, A., Luche, J.L., Petit, A., 1999. Tetrahedron 55, 10851.

Drexhage, K.H., 1976. J. Res. Nat. Bur. Stand A 80A, 8.

Duarte, F.J., Liao, L.S., Vaeth, K.M., Miller, A.M., 2006. J. Opt. A: Pure Appl. Opt. 8, 172.

Eggeling, C., Brand, L., Seidel, C., 2002. Jpn. J. Appl. Phys. 41, 5801.

Fischer, A., Cremer, C., 1995. Stelzer. EHK. Appl. Opt. 34, 1989.

Hausermann, H., Valtz, J., 1961. US 3014041.

Hausermann, H., Valtz, J., 1967. US 3458880.

Holman, R.E., et al., 1984. US 3924929.

Leray, I., Habib-Jiwan, J.L., Branger, C., Soumillion, J.P., Valeur, B., 2000. J. Photochem. Photobiol. 135, 9.

Lew, A., Krutzik, P.O., Hart, M.E., Chamberlin, A.R., 2002. J. Comb. Chem. 4, 95.

Li, Z., Zhang, Z., Emery, T., Scherer, A., Psaltis, D., 2006. Opt. Express 14, 701.

Lidström, P., Tierney, J., Wathey, B., Westman, J., 2001. Tetrahedron 57, 9225.

Loupy, A., 1993. Spectra Anal. 175, 33.

Majetich, G., Hicks, R., 1994. J. Res. Chem. Intermed. 20, 61.

Ohkawa, M., Ishii, K., 1967. US 3933847.

Schwander, H., Hendrix, P., Yamamoto, Y.S., 1988. Ullmann's Encyclopedia of Industrial Chemistry. Weinheim-VCH.

Sokoowska, J., Czajkowski, W., Podsiad, R., 2001. Dyes Pigm. 49, 8.

Strauss, C.R., Trainor, R.W., 1995. Aust. J. Chem. 48, 1665.

Ward, R.A., Kimmel, E.L., 1982. Luminescent materials, third ed.. In: Kirk-Othmer (Ed.), . In: Encyclopedia of Chemical Technology, vol. 14 John Wiley, New York.

Zhao, B., Zhou, Z.H., Shida Xuebao, N., Kexueban, Z., 1982. Chinese Journal of chemistry. 27, 54.