Asian Journal of Chemistry Vol. 22, No. 7 (2010), 5781-5783

NOTE

A Comparative Study of the Synthesis of 6-[(Z)(4-Chlorophenyl) diazenyl]-N-(3,4-dichlorophenyl)-2-oxo-2*H*-chromene-3-carboxamide

MOHAMMED SHAHNAWAAZ*, ARSHI NAQVI, ARIKATLA V. RAO and DAYA S. SETH
Department of Chemistry, School of Chemical Sciences, St. John's College, Agra-282 002, India
E-mail: shaan_organic@yahoo.co.in

The synthesis of 6-[(Z)(4-chlorophenyl)diazenyl]-N-(3,4-dichlorophenyl)-2-oxo-2*H*-chromene-3-carboxamide was achieved from substituted reactive methylene acid in a single step utilizing classical heating, microwave "jump start" and grindstone "friction activated" synthesis.

Key Words: Microwave irradiation, Grinding, Synthesis, Azocoumarin.

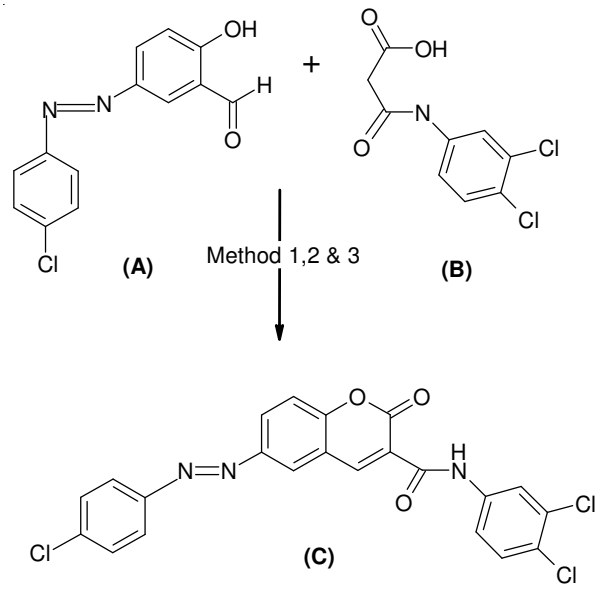
Coumarins are important and well-known naturally occurring oxygen containing heterocyclic compounds. They have shown unique spectrum of activities like antifungal, spasmolytic, bacteriostatic and antitumor[1], anticoagulant[2], antidiuretics and hypertensive[3]. A large number of structurally novel coumarin derivatives have ultimately been reported to show substantial anti HIV activity[4]. Coumarins containing materials are very useful in many fields such as fluorescent materials and laser dyes, photo refractive materials, non linear optical materials, light harvesting materials, alignment layers for liquid crystals *etc*., because of its fluorescence and photodimerization properties[5,6].

Azo compounds have been used for a long time as dyes in industry. Some azo compounds have shown a good antibacterial and antifungal activity[7]. The existence of an azo moiety in different types of compounds has caused them to show herbicidal activity[8]. As a part of our ongoing efforts to develop greener synthetic methods, we have synthesized an azo coumarin (**C**) by changing the sources of energy *i.e*., classical heating, microwave irradiation and friction activated synthesis.

Three different methodologies that were adopted and studied for preparing the title compound are described below:

Classical heating synthesis (method-1): 6-[(Z)(4-chlorophenyl)diazenyl]-N-(3,4-dichlorophenyl)-2-oxo-2*H*-chromene-3-carboxamide (**C**) was synthesized by refluxing 2-hydroxy-5-(4-chloro)phenyl azobenzaldehyde (**A**) (0.001 mol, 0.26 g) and N-3,4-dichlorophenyl malonamic acid (**B**) (0.001 mol, 0.08 g) in presence of 2-3 drops of pyridine and heating for 4 h in an oil bath at 105-110 ºC. The solid product thus obtained was recrystallized from absolute ethanol. m.p. > 300 ºC, yield = 71.34 %.

Microwave "jump start" synthesis (method-2): A mixture of 2-hydroxy-5-(4-chloro)phenyl azobenzaldehyde (**A**) (0.001 mol, 0.26 g) and N-3,4-dichlorophenyl malonamic acid (**B**) (0.001 mol, 0.08 g) and pyridine (0.02 mmol) were taken in a round bottom flask. Reaction mixture was irradiated in microwave oven for 6 min. On cooling the reaction mixture, a good yield of title compound was obtained which was recrystallized from absolute ethanol. m.p. > 300 ºC, yield = 77.86 %.



IR (KBr, ν_{max}, cm^{-1}): 3237 (N-H, stret.), 2921 (lactone ring stret.), 1673 (-C=O stret.), 1620 aromatic (-C=C- stret.), 1570 (-CONH- amide-II stret.), 1475 (-N=N- stret.).

Grindstone 'friction activated' synthesis (method-3): 6-[(Z)(4-chlorophenyl) diazenyl]-N-(3,4-dichlorophenyl)-2-oxo-2*H*-chromene-3-carboxamide (**C**) was synthesized by grinding 2-hydroxy-5-(4-chloro) phenyl azo benzaldehyde (**A**) (0.001 mol, 0.26 g) and N-3,4-dichlorophenyl malonamic acid (**B**) (0.001 mol, 0.08 g) in presence of a drop of catalyst (pyridine) and ethanol (1 mL), in a mortar with a pestle made of porcelain for 25-40 min. The mixture turns pasty after few minutes of grinding. Leave the reaction mixture for overnight. The solid product thus obtained was recrystallized from absolute ethanol. m.p. > 300 ºC, yield = 67.06 %.

IR (KBr, ν_{max}, cm^{-1}): 3218 (N-H, stret.), 2920 (lactone ring stret.), 1670 (-C=O stret.), 1616 aromatic (-C=C- stret.), 1575 (-CONH- amide-II stret.), 1477 (-N=N- stret.). The starting material (**A**) and (**B**) were synthesized according to reported methods[9,10].

Method	Conventional	Microwave	Grindstone
Time (min)	240	6	25-40
Yield (%)	71.34	77.86	67.06

Yellowish orange crystals, m.p. > 300 ºC. IR (KBr, ν_{max}, cm^{-1}): 3209 (N-H, stret.), 2922 (lactone ring stret.), 1668 (-C=O stret.), 1618 aromatic(-C=C- stret.), 1571 (-CONH- amide-II stret.), 1477 (-N=N- stret.), 580 (ArC-Cl stret.). ^{1}H NMR (300 MHz, DMSO-d_6) in δ ppm: δ 2.50 (DMSO), 6.61-7.55 (m, 2H, Ar-H), 7.97 (s, 1H, C'$_4$ (lactone ring), 7.96 (s,1H, C'$_5$), 7.75 (s, 1H, C'$_7$), 7.52 (s, 1H, C'$_8$), 7.84 (d, 2H, Ar-H), 7.81 (d, 2H, Ar-H), 7.72 (s, 1H, Ar-H), 10.21 (s, 1H, CONH). Anal. calcd. (%) for $C_{22}H_{12}N_3O_3Cl_3$: C 55.99, H 2.55, N 8.89; Found (%): C 56.06, H 2.53, N 8.92.

Along with providing energy in the form of heat, the synthesis has been scaled up towards green chemistry domain by circumventing the use of microwave irradiations and friction activated synthesis by grinding. Out of the above adopted methodologies, microwave method has a great virtue. Rapid reactions are one of the attractive features of this protocol.

Moreover, in this protocol, the products obtained are in high yield, pure and easily isolable. In conclusion, from our point of view, microwave irradiation method has been proved here as a better method for the synthesis of 6-[(Z)(4-chlorophenyl)-diazenyl]-N-(3,4-dichlorophenyl)-2-oxo-2*H*-chromene-3-carboxamide and increase in percentage (%) yield is in following order in three different methods: method-3 (grindstone "friction activated" synthesis) < method-1 (classical heating synthesis) < method-2 (microwave "jump start" synthesis).

ACKNOWLEDGEMENTS

The authors thank the Central Drug Research Institute (CDRI), Lucknow for spectral and elemental analysis.

REFERENCES

1. S. Sardari, Y. Mori, K. Horita, R.G. Micetich, S. Nishibe and M. Daneshtalab, *Bioorg. Med. Chem*., **7**, 1933 (1999); R.G. Kalkhambkar, G.M. Kulkarni, C.M. Kamanavalli, N. Premkumar, S.M.Asdaq and C.M. Sun, *Eur. J. Med. Chem.*, **43**, 2178 (2008).
2. Y.L. Garazd, E.M. Kornienko, L.N. Maloshtan, M.M. Garazd and V.P. Khilya, *Chem. Nat. Prod*., **41**, 508 (2005).
3. L.W. Law, *Cancer Res*., **1**, 397 (1941).
4. I. Ikostova, S. Ravela, P. Genova and R. Argirova, *Bioinorg. Chem. Appl.*, 68274 (2006).
5. S.R. Trenor, A.R. Shultz, B.J. Love and T.E. Long, *Chem. Rev*., **104**, 3059 (2004).
6. Y. Tian, E. Akiyama, Y. Nagase, A. Kanazawa, O. Tsutsumi and T. Ikeda, *J. Mater. Chem*., **14**, 3524 (2004).
7. I. Ostromislensky, *J. Am. Chem. Soc*., **56**, 1713 (1934); A.A. Jarrahpour, M. Motamedifar, K. Pakshir, N. Hadi and M. Zarei, *Molecules*, **9**, 815 (2004).
8. S. Samadhiya and A. Halve, *Orient. J. Chem*., **17**, 119 (2001).
9. G. Saxena, A. Chaudhari, A. Naqvi, M. Shahnawaaz and D.S. Seth, *Orient. J. Chem*., **23**, 683 (2007).
10. M. Shahnawaz, A. Naqvi, A.V. Rao and D.S. Seth, *Orient. J. Chem.*, **24**, 701 (2008).

(*Received*: 28 July 2009; *Accepted*: 7 April 2010) AJC-8623