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A facile one-pot synthesis of 14-aryl-14H-dibenzo [a,j] xanthenes catalyzed by glyoxylic acid

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ABSTRACT

A simple and highly efficient method for the synthesis of 14-aryl-14H-dibenzo[a,j] xanthenes derivatives by condensation of substituted benzaldehyde and β-naphthol in presence of catalytic amount of glyoxylic acid (CHOCOOH). The remarkable advantages offered by this method are simple methodology, shorter reactions time and high yields.

KEYWORDS

Dibenzoxanthene;
Glyoxylic acid;
Substituated benzaldehyde;
β-naphthol.

INTRODUCTION

In recent years, much attention has been directed towards the synthesis of xanthene, especially benzoxanthene compounds due to the fact that benzoxanthene compounds posses a variety of biological and therapeutic properties like antiviral[1], antibacterial[2], and anti-inflammatory activities,[3] as well as in photodynamic therapy (PDT)[4] and as antagonists of the paralyzing action of zoxazolamine[5]. Xanthenes are also available from natural sources. Popularly known, Santalin pigments have been isolated from a number of plant species[6]. Furthermore, benzoxanthene are used as dyes[7] and in laser technologies[8]. Many procedures are disclosed to synthesize xanthenes and benzoxanthenes like cyclodehydrations[9], trapping of benzynes by phenols[10], alkylations of hetero atoms[11]. In addition, 14H-dibenzo [a,j]xanthenes and related products are prepared by reaction of β-naphthol with formamide[12] and carbon monoxide[13]. In view of the importance of benzoxanthenes derivatives, many classical methods for the synthesis of benzoxanthenes derivatives were reported[14-17] by conventional heating and refluxing approaches in the presence of organic solvent. These methods, however, involve long reaction time, harsh reaction conditions, and the use of a large quantity of organic solvent and unsatisfactory yields. Therefore, improvements in such syntheses have been sought continuously.

The use of microwave for the synthesis of organic compounds under solvent-free conditions proved to be efficient, safe and environmentally benign technique, with shorter reaction time, high yields, and easier manipulation. Additionally, it can also avoid the use of hazardous and expensive solvents and can be environmentally benign to make manipulations much easier[18].

Glyoxylic acid is a strong acid with extreme wide applications such as deportation of oximes[19], Diels's Alder reaction[20] and very recently, it is used for the synthesis of 1,2 disubstituted benzimidazoles[21]. However, there are no example of the use of Glyoxylic acid as a catalyst for the synthesis of 2,4,5-triarylimidazoles.

EXPERIMENTAL SECTION

All products are known compounds and these physical data, IR and NMR spectra were essentially identical with those of authentic samples. All the reagents and substituated benzaldehydes were obtained from commercial suppliers and were not purified. Melting points were determined in open capillaries apparatus and were uncorrected. The progress of reactions was monitored by TLC. IR spectra were recorded on Perkin-Elmer FT spectrophotometer in KBr disc. NMR spectra were recorded on Varian, 500 MHz spectrophotometer in CDCl3 as a solvent and TMS as an internal standard.

General procedure for the ynthesis of 14-aryl-14H-dibenzo [a, j] xanthenes

A mixture of substituted benzaldehyde (1 mmol), β-naphthol (2 mmol) and Glyoxylic acid (5 mol%) in a Borosil beaker (50 mL) was added. The reaction mixture was mixed properly with the help of a glass rod and irradiated in a microwave oven at 720 W for an appropriate time given in TABLE 1. The progresses of reactions were monitored on TLC. Then crude reaction mixture was cooled to room temperature and treated with ice- cool water. The product was filtered, dried and recrystallized from ethyl alcohol to get pure product.

RESULT AND DISCUSSION

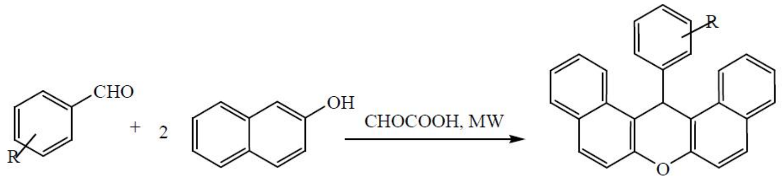
In continuation of our ongoing research for the development of simple and efficient method for the synthesis of benzoxanthenes[22] and various heterocyclic compounds[23], herein we wish to report an efficient, convenient, improved yield and novel method for condensation of substituted benzaldehyde with β-naphthol in presence of glyoxylic acid (5 mol%) as a catalyst (Scheme 1).

Initially, we have carried out a model reaction

TABLE 1 : Glyoxylic acid catalyzed efficient synthesis of 14-aryl-14H-dibenzo [a,j]xanthenes[a]

Entry	R	MW		M.P.(^{0}C)
		Time (sec)	Yield (%)	Found
3a	H	60	92	182
3b	3-F	30	90	260
3c	4-Cl	50	93	287
3d	2-Cl	60	90	215
3e	4-NO_2	90	92	312
3f	3-NO_2	80	90	212
3g	2-NO_2	80	91	292
3h	4-OMe	70	90	203
3i	4-OH	30	90	141
3j	4-Me	50	89	226
3k	2-OMe, 4-OH	50	90	169
3l	2-OMe,5-OMe	20	90	168

[a] **All products were characterized by their physical constant, comparison with authentic samples, and IR, and NMR spectroscopy**[14-17]



1(a-l) 2 3 (a-l)

Scheme 1

of benzaldehyde and β-naphthol using glyoxylic acid (5 mol%), under microwave irradiation operating at 720W power, the reaction proceeded smoothly and was completed within 60 sec of reaction time and 92% conversion. Further increase in the catalyst amount did not show any marked reduce the time and increase in the yield of the reaction. It was observed that 5mol% of glyoxylic acid is quite efficient for the condensation of β-naphthol and substituted benzaldehyde to produce the corresponding xanthenes using microwave irradiation. The reaction was performed with benzaldehyde containing withdrawing as well as electron donating groups, but benzaldehydes with electron donating groups are generally more reactive than their corresponding benzaldehydes with electron withdrawing groups and give the desired product at short reaction time with excellent yield (TABLE 1). This observation shows clearly that the preparation of benzoxanthenes is more strongly affected by the electronic factors.

CONCLUSIONS

In conclusion, we have achieved an facile, efficient, and environment-friendly method for one-pot synthesis of 14-aryl-14H-dibenzo [a,j] xanthenes derivatives using substituted benzaldehyde with β-naphthol in presence of catalytic amount of glyoxylic acid. Products are obtained in shorter reaction times and got the condensed product in good to high yield.

Spectral data for selected compounds:

(11). ^{1}H NMR (CDCl3, 500 MHz)

δ=8.40 (2H, d, J = 8.2 Hz), 7.83 (2H, d, J = 7.8 Hz), 7.79 (2H, d, J = 8.7 Hz), 7.58 (2H, t, J = 7.2 Hz), 7.48 (2H, d, J = 8.7 Hz), 7.42 (2H, t, J = 7.2 Hz), 7.15 (1H, d, J = 8.0 Hz), 6.85 (1H, s), 6.73 (1H, d, J = 8.0 Hz), 6.44 (1H, s), 5.34 (1H, s), 3.65 (3H, s) ppm; ^{13}C NMR (CDCl3): δ= 148.7, 146.7, 144.1, 137.1, 131.4, 131.1, 128.8, 128.7, 126.7, 124.2, 122.7, 121.0, 117.9, 117.5, 113.7,110.7, 55.6, 37.5 ppm; IR (KBr, cm^{-1}): 3477, 2963, 1591, 1509, 1458, 1430, 1401, 1240, 1032, 959, 805, 781, 749.

(12). ^{1}H NMR (CDCl3, 500 MHz)

δ= 8.62 (2H, d, J = 8.4 Hz), 7.82 (2H, d, J = 8.0 Hz), 7.78 (2H, d, J = 8.9 Hz), 7.59 (2H, t, J = 7.3 Hz), 7.50 (2H, d, J = 8.8 Hz), 7.45(2H, t, J = 7.4 Hz), 6.9 (1H, s), 6.84 (1H, s), 6.78 (1H, d, J = 9.0 Hz), 6.48 (1H, d, J = 6.0 Hz), 4.24 (3H, s), 3.47 (3H, s) ppm; ^{13}C NMR (CDCl3): δ= 154.1, 148.8, 148.2, 135.6, 132.0, 129.9, 129.7, 128.6, 128.5, 126.7, 124.2, 123.4, 118.3, 117.0, 111.9,,111.3, 56.1, 55.2, 30.5 ppm; IR (KBr, cm^{-1}): 2925, 2831, 1622, 1594, 1496, 1461, 1430, 1407, 1256, 1207, 1173, 1043, 965, 849, 813, 800, 746, 702.

REFERENCES

[1] R.W.Lambert, J.A.Martin, J.H.Merrett, K.E.B.Parkes, G.Thomas; J.Chem.Abstr, 126 212377y PCT Int App WO 9706178 1997, **(1997)**.

[2] T.J.Hideo, K.Tokkyo; Chem.Abstr., 95 80922b JP 56005480 1981, **(1981)**.

[3] J.P.Poupelin, Saint G.Rut, Foussard O.Blanpin, G.Narcisse, Uchida G.Ernouf, R.Lacroix; Eur.J.Med.Chem., **13**, 67 **(1978)**.

[4] **(a)** R.M.Ion; Progr.Cata., **2**, 55 **(1997)**; **(b)** R.M.Ion, D.Frackowiak, A.Planner, K.Wiktorowicz; Acta.Biochim., **45**, 833 **(1998)**.

[5] Saint G.Ruf, A.De, H.T.Hieu; Bull.Chim.Ther., **7**, 83 **(1972)**; **(b)** Saint G.Ruf, H.T.Hieu, J.P.Poupelin; Naturwissenschaften, **62**, 584 **(1975)**.

[6] J.Kinjo, H.Uemura, T.Nohara, M.Yamashita, N.Marubayashi, K.Yoshihira; Tetrahedron Lett., **36**, 5599 **(1995)**.

[7] S.M.Menchen, S.C.Benson, J.Y.Lam, W.Zhen, D.Sun, B.B.Rosenblum, S.H.Khan, M.Taing; Chem.Abst., **139**, 54287f US Patent US6583168 2003 **(2003)**; **(b)** A.Banerjee, A.K Mukherjee; Stain.Technol., **56**, 83 **(1981)**.

[8] O.Sirkeeioglu, N.Talinli, A.Akar; J.Chem.Res.Synop., **12**, 502 **(1995)**; **(b)** M.Ahmad, T.A.King, Ko K.Do, B.H.Cha, J.Lee; J.Phy.D.Appl.Phys., **35**, 1473 **(2002)**.

[9] R.J.Sarma, J.B.Baruah; Dyes.Pigm., **64**, 91 **(2005)**; **(b)** A.R1.Khosropour, M.M.Khodaei, H.Moghannian; Synlett., **6**, 955 **(2005)**.

[10] D.W.Knight, P.B.Little; J.Chem.Soc.Perkin.Trans.1, **14**, 1771 **(2001)**.

[11] R.Vazquez, de la M.C.Fuentem, L.Castedo, D.Domínguez; Synlett, **433**, **(1994)**; **(b)** H.Ishibashi, K.Takagaki, N.Imada, M.Ikeda; Synlett., **49**, **(1994)**.

[12] P.Papini, R.Cimmarusti; Gazz.Chim.Ital., **77**, 142

(1947).

[13] K.Ota, T.Kito; Bull.Chem.Soc.Jpn., **49**, 1167 **(1976)**.

[14] P.S.Kumara, B.S.Kumara, B.Rajithaa, P.N.Reddya, N.Sreenivasulua, Y.T.Reddy; Arkivoc, **12**, 46 **(2006)**.

[15] B.Das, B.Ravikanth, R.Ramu, K.Laxminarayana, Vittal, B.Rao; J.Mol.Catal.A.Chem., **255**, 74 **(2006)**.

[16] b.Rajitha, Sunil B.Kumar, Thirupathi Y.Reddy, Narsimha P.Reddy, N.Sreenivasulu; Tetrahedron Lett., **46**, 8691 **(2005)**.

[17] R.S.Hamid, G.Majid, M.Nooshin; Arkivoc, **15**, 1 **(2007)**.

[18] **(a)** S.Caddick; Tetrahedron Let., **51**, 10403 **(1995)**; **(b)** A.Katritzky, K.Sandeep, Arkivoc, **13**, 68 **(2003)**; **(c)** C.Khour, C.Darth, A.Lalnger and M.Daves, J.Catal., **149**, 195 **(1994)**.

[19] S.Chavan, P.Soni; Tetrahedron Lett., **45**, 3161 **(2004)**.

[20] A.Jacques, L.Nadege; J.Chem.edu., **75**, 1285 **(1998)**.

[21] S.Pawar, V.Dekhane, M.Shingare, S.Thore; Chin.Chem.Lett., **19**, 1055 **(2008)**.

[22] K.F.Shelke, V.M.Markhele, A.H.Kategaonkar, M.S.Shingare; Bulletin of the catalysis society of India, **6**,136 **(2007)**.

[23] **(a)** S.S.Shindalkar, B.R.Madje, M.S.Shingare; J.Korean.Chem.Soc., **49**, 377 **(2005)**; **(b)** R.V.Hangarge, M.S.Shingare; Mendeleev Commu., **2**, 79 **(2003)**; **(c)** A.S.Gajare, D.P.Sabade, M.S.Shingare, R.D.Wakharkar; Synthetic Commun., **32**, 1549 **(2002)**; **(d)** R.V.Hangarge, M.S.Shingare; Green Chem., **4**, 266 **(2002)**; **(e)** B.R.Madje, S.S.Shindalkar, M.S.Shingare; Ind.J.Hetero.Chem., **14**, 87 **(2004)**.