Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron Letters 47 (2006) 8827–8829
Tetrahedron Letters

Heterogeneous catalyst: Amberlyst-15 catalyzes the synthesis of 14-substituted-14*H*-dibenzo[*a*,*j*]xanthenes under solvent-free conditions

Shengkai Ko and Ching-Fa Yao*

Department of Chemistry, National Taiwan Normal Universtry, 88, Tingchow Road, Taipei 116, Taiwan, ROC

Received 6 July 2006; revised 12 October 2006; accepted 13 October 2006

Abstract—A one-pot condensation of β-naphthol with aldehydes in the presence of Amberlyst-15 to give 14-substituted-14*H*-dibenzo[*a*,*j*]xanthenes under solvent-free condition is described.

The synthesis of xanthene derivatives has been of considerable interest to chemists because of their wide range of biological and pharmaceutical properties such as antiviral,[1] antibacterial,[2] and anti-inflammatory activities.[3] Furthermore, these compounds can be used as dyes,[4] in laser technology,[5] pH-sensitive fluorescent materials for the visualization of biomolecular assemblies.[6] It is also noteworthy that dibenzoxanthenes derivatives are candidates as sensitizers in photodynamic therapy.[7] Thus, the synthesis of benzoxanthene derivatives currently is of great interest. Various methods have been reported for the synthesis of benzoxanthenes, including the reaction of β-naphthol with formamide,[8] 2-naphthol-1-methanol,[9] and carbon monoxide.[10] However, these methods have many disadvantages such as low yields, the need for a prolonged reaction time, the use of toxic organic solvents, excess reagents, and harsh reaction conditions. Because of these drawbacks, the reaction has been improved by mixing β-naphthol with aldehydes in the presence of a catalyst, such as *p*TSA,[11] sulfamic acid,[12] I_2,[13] $AcOH–H_2SO_4$.[14] These methods also suffer from some disadvantages such as a long reaction time, the use of toxic solvent, special apparatus, and the use of toxic catalysts. Thus, the development of a new catalyst for the synthesis of dibenzoxanthene derivatives would be highly desirable.

In recent years, the use of solid acidic catalysts has offered important advantages in organic synthesis, for example, operational simplicity, environmental compatibility, nontoxic, reusability, low cost, and ease of isolation. A tremendous upsurge of interest in various chemical transformations processes by catalysts under heterogeneous conditions has occurred. One of those heterogeneous catalysts is Amberlyst-15. It makes reaction processes convenient, more economic, and environmentally benign. Owing to the numerous advantages associated with this cheap and nonhazardous catalyst, Amberlyst-15 has been explored as a powerful catalyst for various organic transformations under mild conditions,[15] such as the synthesis of bisindoylmethanes, dioxo-octahydroxanthenes, dioxo-decahydroacridines, and 1,2-diaryl-2-bromo-alcohols.

We had the opportunity to further explore the catalytic activity of Amberlyst-15 for the synthesis of 14-substituted-14*H*-dibenzo[*a*,*j*]xanthenes. Herein, we wish to report on a novel synthesis of 14-substituted-14*H*-dibenzo[*a*,*j*]xanthenes in a high yield, promoted by the catalytic amounts of Amberlyst-15 under solvent-free conditions. In an initial endeavor, 1 equiv of benzaldehyde **1a** and 2 equiv of β-naphthol **2** were stirred at 125 °C. After 24 h, only 36% of the expected product **3** was obtained after recrystallizing the crude product from ethanol. To improve the yield and optimize the reaction conditions, the same reaction was carried out in the presence of Amberlyst-15 under similar conditions. Surprisingly, a significant improvement was observed and the yield of **3** was increased to 94%.

Based on the above results, we also conducted the same reactions using aldehydes **1b**–**k** and **2** in the presence of

---

* Corresponding author. Tel./fax: +886 2 29309092; e-mail: cheyaocf@scc.ntnu.edu.tw

0040-4039/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2006.10.072

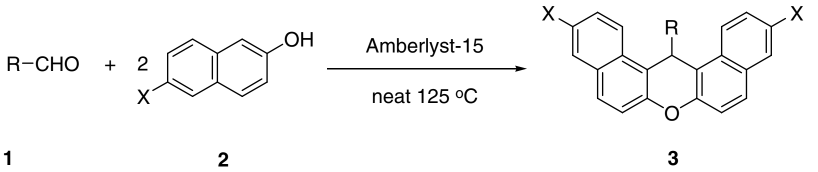
Table 1. Amberlyst-15 catalyzes the synthesis of 14-substitued-14*H*-dibenzo[*a*,*j*]xanthenes under solvent-free conditions[a]

Entry	1	R	X	Time	Yield[b] (%)
1	**1a**	Ph	H	2 h	**3a** (94)
2	**1b**	4-Cl–C_6H_4	H	30 min	**3b** (82)
3	**1c**	2-Cl–C_6H_4	H	20 min	**3c** (91)
4	**1d**	4-F–C_6H_4	H	1 h	**3d** (94)
5	**1e**	3-F–C_6H_4	H	1 h	**3e** (90)
6	**1f**	4-Me–C_6H_4	H	1 h	**3f** (91)
7	**1g**	3-CF_3–C_6H_4	H	30 min	**3g** (82)
8	**1h**	$PhCH_2$	H	2 h	**3h** (80)
9	**1i**	$(CH_3)_2CHCH_2$	H	1 h	**3i** (83)
10	**1j**	4-CF_3–C_6H_4	H	0.5 h	**3j** (89)
11	**1k**	3-CF_3–C_6H_4	Br	2 h	**3k** (89)

[a] Aldehyde–β-napthol = 1mmol:2 mmol.

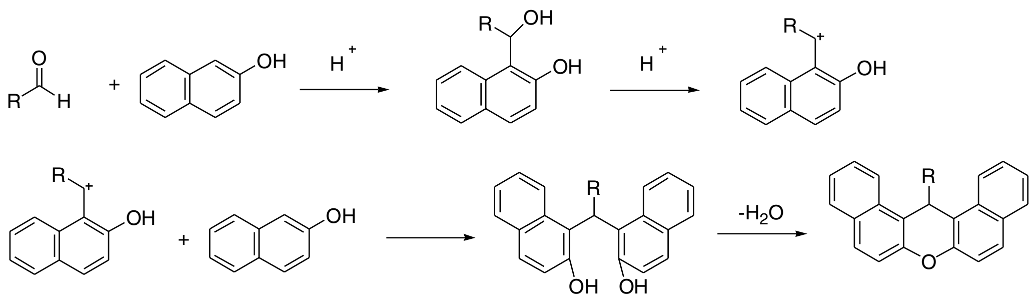
[b] Isolated yield.

Amberlyst-15 under similar conditions. As expected, satisfactory results were observed and the results are summarized in Eq. 1 and Table 1.



(1)

Concerning the reaction mechanism, we proposed that a carbocation is initially formed, aryl- or alkyl-methane-bisnaphthols are then formed in the second step, which then undergo dehydration to give the final product which is similar to the literature reports.[16] Because an electron-withdrawing group cannot stabilize an intermediate carbocation, the reaction was more active and the yield was less, when an electron-donating group is present. On the contrary, electron-donating group can stabilize the carbocation, so the reaction was mild and the yield is higher. Alkyl aldehydes are more active than aryl aldehydes and the yield of product is intermediate.



In conclusion, we successfully developed a facile and efficient method for preparing a variety of 14-substituted-14*H*-dibenzo[*a*,*j*]xanthenes by the reactions of various aldehydes with β-naphthol in the presence of a catalytic amount of Amberlyst-15 under solvent-free conditions. The catalytic activity of Amberlyst-15 is remarkable and it is environmentally benign, and commercially available. The fact that Amberlyst-15 catalyzes the synthesis of 14-substituted-14*H*-dibenzo[*a*,*j*]xanthenes in good yields is also significant. The advantages such as shorter reaction times, milder conditions, simplicity of the reaction, good product yields, and the relatively straightforward procedures involved in the reaction makes the inexpensive and commercially available Amberlyst-15 a powerful catalyst for the synthesis of different organic compounds.

Acknowledgment

Financial support of this work from the National Science Council of the Republic of China is gratefully acknowledged.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.10.072.

References and notes

1. Lambert, R. W.; Martin, J. A.; Merrett, J. H.; Parkes, K. E. B.; Thomas, G. J. *Chem. Abstr.* **1997**, *126*, p212377y, PCT Int. Appl. WO 9706178, 1997.
2. Hideo, T. *Chem. Abstr.* **1981**, *95*, 80922b, Jpn. Tokkyo Koho JP 56005480, 1981.
3. Poupelin, J. P.; Saint-Rut, G.; Foussard-Blanpin, O.; Narcisse, G.; Uchida-Ernouf, G.; Lacroix, R. *Eur. J. Med. Chem.* **1978**, *13*, 67.

4. (a) Banerjee, A.; Mukherjee, A. K. *Stain Technol.* **1981**, *56*, 83; (b) Menchen, S. M.; Benson, S. C.; Lam, J. Y. L.; Zhan, W.; Sun, D.; Rosenblum, B. B.; Khan, S. H.; Ting, M. U.S. Patent, US 6583168, 2003.
5. (a) Sirkeeioglu, O.; Talinli, N.; Akar, A. *J. Chem. Res. (S)* **1995**, 502; (b) Ahmad, M.; King, T. A.; Ko, Do.-K.; Cha, B. H.; Lee, J. *J. Phys. D: Appl. Phys.* **2002**, *35*, 1473.
6. Knight, C. G.; Stephens, T. *Biochem. J.* **1989**, *258*, 683.
7. Ion, R. M.; Sirkecioglu, O.; Talinli, N. The spectroscopy and associated photodynamic derivatives, The Third Internet Conference on Photobiology.
8. Papini, P.; Cimmarusti, R. *Gazz. Chim. Ital.* **1947**, *77*, 142.
9. Sen, R. N.; Sarkar, N. *J. Am. Chem. Soc.* **1925**, *47*, 1079.
10. Ota, K.; Kito, T. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1167.
11. Khosropour, A. R.; Khodaei, M. M.; Moghannian, H. *Synlett* **2005**, 955.
12. Rajitha, B.; Kumar, B. S.; Reddy, Y. T.; Reddy, P. N.; Sreenivasulu, N. *Tetrahedron Lett.* **2005**, *46*, 8691.
13. Das, B.; Ravikanth, B.; Ramu, R.; Laxminarayana, K.; Rao, B. V. *J. Mol. Catal. A: Chem.* **2006**, *255*, 74.
14. Sarma, R. J.; Baruah, J. B. *Dyes Pigments* **2005**, *64*, 91.
15. (a) Ballini, R.; Petrini, M. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2563; (b) Ramesh, C.; Banerjee, J. R.; Pal, B. D. *Adv. Synth. Catal.* **2002**, *345*, 557; (c) Yu, W.; Hidajat, K.; Ray, A. K. *Appl. Catal. A: Gen.* **2004**, *260*, 191; (d) Feng, X.-L.; Guan, C.-J.; Zhao, C.-X. *Synth. Commum.* **2004**, *34*, 487; (e) Farhanullah; Ashoke, S.; Maulik, P. R.; Ram, V. J. *Tetrahedron Lett.* **2004**, *45*, 5099; (f) Ke, B.; Qin, Y.; He, Q.; Huang, Z.; Wang, F. *Tetrahedron Lett.* **2005**, *46*, 1751; (g) Solladie-Cavallo, A.; Lupattelli, P.; Bonini, C. *J. Org. Chem.* **2005**, *70*, 1605; (h) Das, B.; Thirupathi, P.; Mahender, I.; Reddy, V. S.; Rao, Y. K. *J. Mol. Catal. A: Chem.* **2006**, *255*, 233.
16. (a) Rashidi-Ranjbar, P.; Mohajeri, A.; Mahmoudkhani, A. H. *J. Phys. Org.* **2001**, *14*, 210; (b) Khoramabadi-zad, A.; Kazemi, Z.; Rudbari, H. A. *J. Korean Chem. Soc.* **2002**, *46*, 541.