Synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives catalysed by expanded graphite under solvent-free condition

Geng-Chen Li*

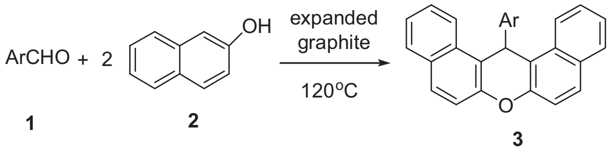
School of Material Science and Engineering, Shijiazhuang Railway Institute, Shijiazhuang 050043, China

A convenient eco-friendly procedure has been developed for the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives by one-pot condensation of 2-naphthol and aryl aldehydes catalysed by expanded graphite under solvent-free conditions. The present methodology offers several advantages such as excellent yields, shorter reaction times, low cost and reusability of the catalyst.

Keywords: xanthene, 2-naphthol, aldehydes, expanded graphite, solvent-free conditions

The application of heterogeneous acid catalysts in place of homogeneous acid catalysts in organic transformations is an attractive area of research.[1-4] The advantages of heterogeneous catalysts over homogeneous catalysts include stability, lack of corrosion, ease of handling, recovery and regeneration. Expanded graphite (EG) is a new biomedical material,[5] which can be used as a catalyst and a novel carbon support material.[6] It has been reported to be an efficient catalyst for many important organic transformations.[9-13]

Xanthenes and their derivatives are important biologically-active heterocyclic compounds.[14-15] Furthermore, these compounds can be employed as dyes, pH-sensitive fluorescent materials and in laser technology.[16] Hence, the synthesis of a variety of xanthenes is an important objective. Various methods have been developed for the preparation of such compounds.[17] In spite of the potential utility of these routes, many of these methods involve expensive reagents and complex methodology. Recently, several improved procedures have been reported for the synthesis of 14*H*-dibenzo[*a,j*]xanthene by condensation of 2-naphthol and aldehydes in the presence of toluenesulfonic acid,[18] methanesulfonic acid,[19] *p*-dodecylbenzenesulfonic acid (DBSA),[20] $Al(HSO_4)_3$,[21] $NaHSO_4$,[22] iodine,[23] $NaHSO_4·SiO_2$,[24] Amberlyst-15,[25] perchloric acid-silica,[26] dipyridinecobalt chloride,[27] dipyridinecopper chloride,[28] or tetra-*n*-butylammonium bromide (TBAB)[29] as catalyst. However, some of these catalysts are toxic, difficult to prepare and are expensive. The development an efficient and environmentally benign synthetic method to overcome these limitation is still an important challenge. In continuation of our interest on the application of cheap and eco-friendly materials as catalysts for development of useful synthetic methodology,[31-32] we now report a novel and high yielding method for the preparation of 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives using expanded graphite as an eco-friendly catalyst under solvent-free conditions (Scheme 1).



Scheme 1

Initially, the effective amount of expanded graphite as catalyst was investigated for the model reaction of 3-nitrobenzaldehyde (**1o**, 1 mmol) and 2-naphthol (2 mmol) at 120 °C under solvent-free conditions. The reaction rate and yield increased with the amount of the catalyst. It was found that 50 mg of catalyst was the appropriate amount for the reaction. A smaller amount gave a low yield even after a long reaction time. A higher amount did not lead to an increase in the yield of the product. In the absence of catalyst, the model reaction gave only a trace of the product even after a long time (6 h). Lower temperatures were used but required a longer reaction time.

Table 1 Synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives catalysed by expanded graphite

Entry	Aldehydes	Time/h	Yield/%[a]	Mp/°C	
				Found	Reported
a	PhCHO	1.5	90	182–183	183[27]
b	$3\text{-}MeOC_6H_4CHO$	2	92	181–183	180–181[19]
c	$4\text{-}MeOC_6H_4CHO$	2	91	206–208	205[27]
d	$4\text{-}MeC_6H_4CHO$	3	90	228–230	228[27]
e	$3,4\text{-}(OCH_2O)C_6H_3CHO$	2	89	239–240	240–241[20]
f	$3\text{-}MeO\text{-}4\text{-}OHC_6H_3CHO$	2	88	210–212	208–210[19]
g	$3\text{-}FC_6H_4CHO$	1.5	92	255–257	258–259[27]
h	$4\text{-}FC_6H_4CHO$	1.5	91	236–238	238[27]
i	$2\text{-}ClC_6H_4CHO$	2	90	215–216	215[27]
j	$4\text{-}ClC_6H_4CHO$	1	95	288–289	287[27]
k	$2,4\text{-}Cl_2C_6H_3CHO$	2	91	228–230	228[21]
l	$3\text{-}BrC_6H_4CHO$	1	94	190–192	190[27]
m	$4\text{-}BrC_6H_4CHO$	1	95	296–298	296[27]
n	$2\text{-}NO_2C_6H_4CHO$	2	88	290–291	293[27]
o	$3\text{-}NO_2C_6H_4CHO$	1	95	215–216	213[27]
p	$4\text{-}NO_2C_6H_4CHO$	1	94	310–312	312[27]
q	$4\text{-}CNC_6H_4CHO$	1.5	91	335–336	
r	2-Naphthalenecarbaldehyde	1.5	92	200–201	

[a] Isolated yield.

---

* Correspondent. E-mail: gengchenli@sina.com.cn

Having established the optimum experimental conditions, various 14-aryl-14*H*-dibenzo[*a,j*]xanthenes were synthesised in good to excellent yields by the reaction of different aromatic aldehydes with 2-naphthol. Representative examples are summarised in Table 1. As shown in Table 1, present methodology worked efficiently with a wide variety of substrates. In all cases, the 14-aryl-14*H*-dibenzo[*a*,j]xanthene was the sole product and no by-products were observed. Aromatic aldehydes with electron-withdrawing groups reacted faster than the aromatic aldehydes with electron-releasing groups as would be expected. Sterically hindered aromatic aldehydes such as 2-chloro (**1i**) and 2-nitro (**1n**) bezaldehydes required long reaction times. 2-Naphthalene-carbaldehyde (**1r**) was also examined under these conditions and gave the corresponding product in excellent yield. Another important aspect is that various functionalities such as halide, nitro, and hydroxyl, survived under the present reaction conditions.

Recycling of the catalyst was also investigated. After completion of the model reaction, the mixture was washed with ethyl acetate and the catalyst was filtered, and activated at 100 °C for 2 h and reused in another reaction with the same substrates. The catalyst could be reused at least three times without appreciable decrease in yield and reaction rate.

In summary, an environmentally friendly procedure for the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthene derivatives by one-pot condensation of 2-naphthol and aryl aldehydes catalysed by expanded graphite has been developed. This method has several merits, involving a simple experimental procedure, solvent-free conditions, short reaction times, high yield of product, general applicability and it uses an inexpensive and recyclable catalyst.

Experimental

IR spectra were obtained as KBr pellets with a Thermo Nicolet FT-IR200 spectrometer. NMR spectra were recorded on a Bruker AV 300 spectrometer in $CDCl_3$ using TMS as an internal standard. The melting points are uncorrected and were recorded on a WRR melting point instrument. Elemental analyses were performed on a PE 2400 CHNS/O Analyser.

The preparation of expanded graphite: A mixture of concentrated sulfuric acid (98%, 20 g), nitric acid (65%, 10 g), natural flake graphite (10 g) and potassium permanganate (0.7 g) was stirred at room temperature for 30 min. The expanded graphite was filtered, washed with water until pH = 6–7 and dried at 6 C for 1 h.[9]

General procedure for the synthesis of 14-aryl-14H-dibenzo[a,j]xanthene derivatives: 2-Naphthol (2 mmol), aldehydes (1 mmol) and expanded graphite (50 mg) were ground well and transferred to a 25 ml flask and the mixture was inserted in an oil bath and heated at 120 °C for an appropriate time (monitored by TLC). After completion of the reaction, the mixture was cooled to room temperature, washed with ethyl acetate and the catalyst was filtered. The solvent was evaporated and the crude products were purified by recrystallisation from aqueous ethanol to afford the pure product.

14-(4-Methoxy-phenyl)-14H-dibenzo[a,j]xanthene (**3c**): IR (KBr): 3041 (=C–H), 2923 (CH), 1605 (C=C), 1508 (C=C), 1249 (C–O–C) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ ppm: 3.63 (s, 3H), 6.60 (s, 1H), 6.70 (d, *J* = 8.7 Hz, 2H), 7.38–7.48 (m, 6H), 7.56–7.82 (m, 6H), 8.38 (d, *J* = 8.7 Hz, 2H). Anal. Calcd. for $C_{28}H_{20}O_2$: C, 86.57; H, 5.19. Found: C, 86.35; H, 5.42%.

14-(2-Nitro-phenyl)-14H-dibenzo[a,j]xanthene (**3n**): IR (KBr): 3398 (=C–H), 1592 (C=C),, 1521 (N = O), 1348 (N = O), 1254 (C–O–C) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ ppm: 7.50 (s, 1H), 7.08–7.64 (m, 10H), 7.78–7.82 (m, 4H), 8.50 (d, *J* = 8.1 Hz, 2H). Anal. Calcd. for $C_{27}H_{17}NO_3$: C, 80.38; H, 4.25; N, 3.47. Found: C, 80.12; H, 4.40; N, 3.65%.

4-(14H-Dibenzo[a,j]xanthen-14-yl)-benzonitrile (**3q**): IR (KBr): 2870 (CH), 2225 (C≡N), 1590 (C=C), 1505 (C=C), 1243 (C–O–C) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ ppm: 6.55 (s, 1H), 7.40–7.82 (m, 14H), 8.25 (d, *J* = 8.7 Hz, 2H). Anal. calcd. For $C_{28}H_{17}NO$: C, 87.71; H, 4.47; N, 3.65. Found: C, 87.81; H, 4.65; N, 3.56%.

14-Naphthalen-2-yl-14H-dibenzo[a,j]xanthene (**3r**): IR (KBr): 3046 (=C–H), 1588 (C=C), 1244 (C–O–C) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ ppm: 7.08 (s, 1H), 7.18–7.48 (m, 9H), 7.68–8.46 (m, 9H), 9.10 (d, *J* = 8.7 Hz, 1H). Anal. calcd. For $C_{31}H_{20}O$: C, 91.15; H, 4.93. Found: C, 91.06; H, 4.84%.

This research was financially supported in part by the Science and Technology Research and Development Program from Hebei Province (06213507D-2).

Received 15 June 2008; accepted 6 July 2008
Paper 08/5328 doi: 10.3184/030823408X340771
Published online: 26 August 2008

References

1 G. Sartori and R. Maggi, *Chem. Rev*., 2006, **10**6, 1077.
2 J.H. Clark, *Acc. Chem. Res*., 2002, **35**, 791.
3 Z.-H. Zhang and L.-M. Song, *J. Chem. Res*., 2005, 817.
4 Z.-S. Cui, Z.-H. Zhang and S.-F. Liu, *J. Chem. Res*., 2006, 390.
5 W.C. Shen, S.Z. Wen, N.Z. Cao, L. Zheng, W. Zhou, Y.J. Liu and J.L. Gu, *Carbon*, 1999, **37**, 356.
6 W. Li, C. Han, W. Liu, M.H. Zhang and K.Y. Tao, *Catal. Today*, 2007, **125**, 278.
7 Z.-H. Zhang, T.-S. Li, T.-S. Jin and J.-X. Wang, *J. Chem. Res. (S)*, 1998, 152.
8 T.-S. Jin, Y.-R. Ma, Z.-H. Zhang and T.-S. Li, *Synth. Commun*., 1997, **27**, 3379.
9 J.-T. Li, H.-J. Zang, J.-Y. Feng, L.-J. Li and T.-S. Li, *Synth. Commun*., 2001, **31**, 653.
10 T.-S. Jin, G.-Y. Du, Z.-H. Zhang and T.-S. Li, *Synth. Commun*., 1997, **27**, 2261.
11 T.-S. Jin, T.-S. Li and Y.-T. Gao, *Synth. Commun*., 1998, **28**, 837.
12 T.-S. Jin, T.-S. Li, Z.-H. Zhang and Y.-J. Yuan, *Synth. Commun*., 1999, **29**, 1601.
13 Y.-Q. Zhang, C. Wang, G.-S. Li, J.-C. Li, H.-M. Liu and Q.-H. Wu, *Chin. J. Org. Chem*., 2005, **25**, 1265.
14 J.-J. Li, X.-Y. Tao and Z.-H. Zhang, *Phosphorus, Sulfur, and Silicon*, 2008, **183**, 1672.
15 Z.-H. Zhang and X.-Y. Tao, *Aust. J. Chem*., 2008, **61**, 77.
16 B. Das, K. Laxminarayana, M. Krishnaiah and Y. Srinivas, *Synlett*, 2007, 3107.
17 M.M. Amini, M. Seyyedhamzeh and A. Bazgir, *Appl. Catal. A: Gen*., 2007, **323**, 242.
18 A. Khoramabadi-zad, S.-A. Akbari, A. Shiri and H. Veisi, *J. Chem. Res*., 2005, 277.
19 A.K. Bhattacharya and K.C. Rana, *Mendeleev Commun*., 2007, **17**, 247.
20 T.-S. Jin, L.-B. Liu, Y. Yin, Y. Zhao and T.-S. Li, *Lett. Org. Chem*., 2006, **3**, 591.
21 H.R. Shaterian, M. Ghashang and N. Mir, *Arkivoc*, 2007, **xv**, 1.
22 Z. Karimi-Jaberi and M.M. Hashemi, *Monatsh. Chem*., 2008, **139**, 605.
23 B. Das, B. Ravikanth, R. Ramu, K. Laxminarayana and B.V. Rao, *J. Mol. Catal. A: Chem*., 2006, **255**, 74.
24 L. Nagarapu, M.B. Baseeruddin, N.V. Kumari, S. Kantevari and A.P. Rudradas, *Synth. Commun*., 2007, **37**, 2519.
25 S. Ko and C.-F. Yao, *Tetrahedron Lett*., 2006, **47**, 8827.
26 B. Das, D.N. Kumar, K. Laxminarayana and B. Ravikanth, *Helv. Chim. Acta*, 2007, **90**, 1330.
27 J.V. Madhav, B.S. Kuarm and B. Rajitha, *Arkivoc*, 2008, **ii**, 204.
28 J.V. Madhav, V.N. Kumar, P. Someshwar and B. Rajitha, *J. Heterocyclic Chem*., 2008, **45**, 119.
29 S. Kantevari, M.V. Chary, A.P.R. Das, S.V.N. Vuppalapati and N. Lingaiah, *Catal. Commun*., 2008, **9**, 1575.
30 M.A. Bigdeli, M.M. Heravi and G.H. Mahdavinia, *Catal. Commun*., 2007, **8**, 1595.
31 G.-C. Li, *J. Chem. Res*., 2007, 696.
32 G.-C. Li, *Monatsh. Chem*., 2008, **139**, 789.