

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Organic Preparations and Procedures International

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t902189982>

### SYNTHESIS OF ARYL 14H-DIBENZO[A,J]XANTHENES USING ZIRCONIUM(IV) OXIDE CHLORIDE AS A CATALYST

Elaheh Mosaddegh<sup>a</sup>; Mohammad Reza Islami<sup>a</sup>

<sup>a</sup> Department of Chemistry, Shahid Bahonar University of Kerman, Kerman, IRAN

**To cite this Article** Mosaddegh, Elaheh and Islami, Mohammad Reza(2008) 'SYNTHESIS OF ARYL 14H-DIBENZO[A,J]XANTHENES USING ZIRCONIUM(IV) OXIDE CHLORIDE AS A CATALYST', *Organic Preparations and Procedures International*, 40: 6, 586 – 589

**To link to this Article:** DOI: 10.1080/00304940809458126

**URL:** <http://dx.doi.org/10.1080/00304940809458126>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

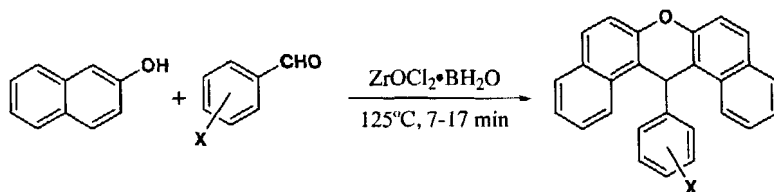
**SYNTHESIS OF ARYL 14H-DIBENZO[a,j]XANTHENES  
USING ZIRCONIUM(IV) OXIDE CHLORIDE AS A CATALYST**

Submitted by Elaheh Mosaddegh and Mohammad Reza Islami\*  
(08/06/08)

*Department of Chemistry, Shahid Bahonar University of Kerman,  
Kerman 76169, IRAN  
e-mail: mrislami@mail.uk.ac.ir*

Xanthenes have attracted considerable attention in recent years,<sup>1-4</sup> being useful as dyes,<sup>5</sup> fluorescent material for visualization of biomolecules<sup>6</sup> and in laser technologies.<sup>7</sup> These materials have also shown anti-bacterial, anti-viral and anti-inflammatory activities.<sup>8-10</sup> Various procedures are available to synthesis xanthenes by cyclization of polycyclic aryltriflate esters,<sup>11</sup> intramolecular trapping of benzynes by phenols,<sup>12</sup> reaction of aryloxymagnesium halides with triethylorthoformate<sup>13</sup> and cyclization between 2-hydroxy aromatic aldehydes and 2-tetralone.<sup>14</sup> Recently, the synthesis of xanthene derivatives has been reported by the condensation of 2-naphthol with aldehydes in the presence of various catalysts.<sup>15-19</sup> However, there are disadvantages to these mentioned methods such as low yield, difficulty in the preparation of the starting materials, prolonged reaction time and use of toxic organic solvents. Thus, a search for new reagents and the development of new methods are still of practical importance. The greatly enhanced reactivity of zirconium(IV) oxide chloride ( $ZrOCl_2 \cdot 8H_2O$ ) led to its emergence as a promising Lewis acid catalyst<sup>20</sup> for reactions such as Michael addition of amines and of indoles to  $\alpha,\beta$ -unsaturated ketones,<sup>21</sup> the condensation of indoles with carbonyl compounds,<sup>22</sup> the synthesis of aryloxazolines<sup>23</sup> and the acylation of alcohols, phenols, amines and thiols.<sup>24</sup>  $ZrOCl_2 \cdot 8H_2O$  is a moisture-stable compound with a shelf-life of several years under laboratory conditions, easy to handle, readily available, and of low toxicity.

In continuation of our interest on the application of heterogeneous catalysts<sup>25,26</sup> for development of useful synthetic methodology,<sup>27</sup> the reaction of *p*-chlorobenzaldehyde with 2-naphthol in the presence of a catalytic amount of  $ZrOCl_2 \cdot 8H_2O$  as a model reaction was investigated. As shown in *Table 1*, in the course of this study it was found that the reaction under thermal conditions at 125°C was best in terms of yield of the corresponding benzoxanthene (96%).



- a) X = 4-NO<sub>2</sub>; b) X = 3-NO<sub>2</sub>; c) X = H; d) X = 3-Cl; e) X = 4-CH<sub>3</sub>; f) X = 2,4-Cl<sub>2</sub>; g) X = 4-Br;  
h) X = 2-Cl; i) X = 3-Br; j) X = 4-Cl; k) X = 3-CH<sub>3</sub>; l) X = 3-HO

**Table 1.** Optimization of Conditions for the Condensation of *p*-Chlorobenzaldehyde with 2-Naphthol.

Entry	Conditions	Time	Yield (%)
1	Solvent: 1,2-dichloroethane, r.t.	24 h	14
2	Solvent: 1,2-dichloroethane, reflux	1 h	25
3	Solvent free, r.t.	24 h	16
4	Solvent free, heat (125°C)	12 min	96

Comparison of the reaction time and the yield of 14-(4-chloro)-14H-dibenzo[a,j]xanthenes with those reported in the literature makes it clear, our method is simpler, more efficient, requires less time and catalyst. The reactions of various aromatic aldehydes under thermal conditions are summarized in *Table 2*. Steric hindrance seems to have no significant effects on the yields. In addition, it was found that  $ZrOCl_2 \cdot 8H_2O$  can be reused several times without loss of activity, simply by filtering the catalyst, washing with dichloromethane and drying at 60°C.

In conclusion, we successfully developed a facile and efficient method for preparing a variety of 14H-dibenzoxanthene derivatives by condensation of various aromatic aldehydes with 2-naphthol in the presence of a catalytic amount of  $ZrOCl_2 \cdot 8H_2O$  under thermal conditions.

**Table 2.** Preparation of Dibenzoxanthenes from Aromatic Aldehydes using  $ZrOCl_2 \cdot 8H_2O$  as Catalyst under thermal Conditions.

Cmpd	Yield <sup>a</sup> (%)	mp. (°C)	lit. mp. (°C)	Time (min)	Ref
<b>1a</b>	93	310-311	310-312	16	2-4,15,17-19
<b>1b</b>	95	210-211	211	14	2-4,15,19
<b>1c</b>	90	182-183	181-183	15	1-4,15,17-19
<b>1d</b>	94	289-290	290-291	12	4,19
<b>1e</b>	92	229-230	229	16	1-4,15,17-19
<b>1f</b>	92	253-255	253-255	12	4,19
<b>1g</b>	95	296-297	297	10	3,15,17-19
<b>1h</b>	95	213-215	215-216	14	1,3,15,18,19
<b>1i</b>	94	192-193	198	13	3,15
<b>1j</b>	96	289-290	290	12	1-4,15,18,19
<b>1k</b>	93	196-197	197-198	17	18
<b>1l</b>	96	262-263	261-263	7	19

<sup>a</sup> Yield of isolated product

## EXPERIMENTAL SECTION

Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. NMR spectra were recorded at 500 ( $^1\text{H}$ ) and 125.77 ( $^{13}\text{C}$ ) MHz on a Bruker DRX-500 Avance spectrometer at 500 and 125.77 MHz, respectively. All compounds were known in the literature, the NMR and IR spectra of the products were in agreement with earlier data.

**Representative Procedure.**- A mixture of 4-chlorobenzaldehyde (0.28 g, 2 mmol), 2-naphthol (0.57 g, 4 mmol) and  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (12 mg, 2 mol%) was stirred at 125°C for 12 min. Completion of the reaction mixture was indicated by TLC (hexane-dichloromethane, 3:1). The reaction was cooled to 25°C and dichloromethane (10 mL) was added and then the mixture stirred for 5 min. The catalyst was separated by filtration. The solvent was removed by distillation and the solid obtained was recrystallized from ethanol and characterized by IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR.

## REFERENCES

1. S. Ko and C. F. Yao, *Tetrahedron Lett.*, **47**, 8827 (2006).
2. B. Das, B. Ravikanth, R. Ramu, K. Laxminarayana and B. V. Rao, *J. Mol. Catal. A Chem.*, **255**, 74 (2006).
3. S. B. Patil, R. P. Bhat and S. D. Samant, *Synth. Commun.*, **36**, 2163 (2006).
4. H. R. Shaterian, M. Ghashang and A. Hassankhani, *Dyes Pigments*, **76**, 564 (2008).
5. a) A. Banerjee and A. K. Mukherjee, *Stain Technol.*, **56**, 83 (1981). b) S. M. Menchen, S. C. Benson, J. Y. L. Lam, W. Zhan, D. Sun, B. B. Rosenblum, S. H. Khan and M. Ting, U. S. Patent, US 6583168 2003; *Chem. Abstr.*, **139**, 54287f, (2003).
6. C. G. Knight and T. Stephens, *Biochem. J.*, **258**, 683 (1989).
7. a) O. Sirkecioglu, N. Talinli and A. Akar, *J. Chem. Res. (S)*, **502** (1995). b) M. Ahmad, T. A. King, Do-K. Ko, B. H. Cha and J. Lee, *J. Phys. D Appl. Phys.*, **35**, 1473 (2002).
8. T. Hideo, Jpn Tokkyo Koho JP 19815 6005480; *Chem. Abstr.*, **95**, 80922b, (1981).
9. R. W. Lambert, J. A. Martin, J. H. Merrett, K. E. B. Parkes and G.J Thomas, PCT. Int. Appl. WO9706178, 1997; *Chem. Abstr.*, **126**, p212377y, (1997).
10. J. P. Poupelin, G. Saint-Rut, O. Foussard-Blanpin, G. Narcisse, G. Uchida-Ernouf and R. Lacroix, *Eur. J. Med. Chem.*, **13**, 67 (1978).
11. J. Q. Wang and R. G. Harvey, *Tetrahedron.*, **58**, 5927 (2002).
12. a) D. W. Knight and P. B. Little, *J. Chem. Soc. Perkin I*, 1771 (2001). b) D. W. Knight and P. B. Little, *Synlett*, 1141 (1998).

13. G. Casiraghi, G. Casnati, M. Catellani and M. Cornia, *Tetrahedron Lett.*, **14**, 679 (1973).
14. A. Jha and J. Beal, *Tetrahedron Lett.*, **45**, 8999 (2004).
15. A. R. Khosropour, M. M. Khodaei and H. Moghannian, *Synlett.*, **10**, 955 (2005).
16. M. A. Bigdeli, M. M. Heravi and G. H. Mahdavian, *Catal. Commun.*, **8**, 1595 (2007).
17. R. J. Sarma and J. B. Baruah, *Dyes Pigments.*, **64**, 91 (2005).
18. M. A. Pasha and V. P. Jayashankara, *Bioorg. Med. Chem. Lett.*, **17**, 621 (2007).
19. L. Nagarapu, S. Kantevari, V. C. Mahankhali and S. Apuri, *Catal. Commun.*, **8**, 1173 (2007).
20. F. Matloubi-Moghaddam, H. Islami and Gh. Rezanejade-Bardajee, *Heteroatom Chem.*, **17**, 136 (2006).
21. H. Firouzabadi, N. Iranpoor, M. Jafarpour and A. Ghaderi, *J. Mol. Catal. A Chem.*, **252**, 150 (2006).
22. H. Firouzabadi, N. Iranpoor, M. Jafarpour and A. Ghaderi, *J. Mol. Catal. A Chem.*, **253**, 249 (2006).
23. I. Mohammadpoor-Baltork, A. R. Khosropour and S. F. Hojati, *Catal. Commun.*, **8**, 200 (2007).
24. R. Ghosh, S. Maiti and A. Chakraborty, *Tetrahedron Lett.*, **46**, 147 (2005).
25. V. Polshettiwar and R. S. Varma, *Acc. Chem. Res.* **41**, 629 (2008).
26. S. Dasgupta and B. Torok, *Org. Prep. Proced. Int.* **40**, 1 (2008).
27. E. Mosaddegh, M. R. Islami and A. Hassankhani, *Lett. Org. Chem.*, **4**, 524 (2007).

\*\*\*\*\*