This article was downloaded by: [Massachusetts Institute of Technology]
On: 04 November 2014, At: 09:24
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: The New Journal for Organic Synthesis
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/uopp20

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

Elaheh Mosaddegh [a] & Mohammad Reza Islami [a]
[a] Department of Chemistry , Shahid Bahonar University of Kerman , Kerman, 76169, IRAN E-mail:

Published online: 18 Feb 2009.

To cite this article: Elaheh Mosaddegh & Mohammad Reza Islami (2008) SYNTHESIS OF ARYL 14H-DIBENZO[A,J]XANTHENES USING ZIRCONIUM(IV) OXIDE CHLORIDE AS A CATALYST, Organic Preparations and Procedures International: The New Journal for Organic Synthesis, 40:6, 586-589, DOI: 10.1080/00304940809458126

To link to this article: http://dx.doi.org/10.1080/00304940809458126

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

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

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

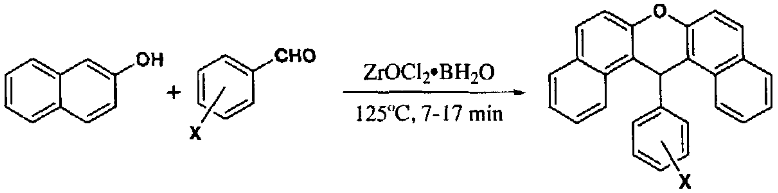
Submitted by (08/06/08)

Elaheh Mosaddegh and Mohammad Reza Islami*

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,[1-4] being useful as dyes,[5] fluorescent material for visualization of biomolecules[6] and in laser technologies.[7] These materials have also shown anti-bacterial, anti-viral and anti-inflammatory activities.[8-10] Various procedures are available to synthesis xanthenes by cyclization of polycyclic aryltriflate esters,[11] intramolecular trapping of benzynes by phenols,[12] reaction of aryloxymagnesium halides with triethylorthoformate[13] and cyclization between 2-hydroxy aromatic aldehydes and 2-tetralone.[14] Recently, the synthesis of xanthene derivatives has been reported by the condensation of 2-naphthol with aldehydes in the presence of various catalysts.[15-19] 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 ($ZrOCl_2$•$8H_2O$) led to its emergence as a promising Lewis acid catalyst[20] for reactions such as Michael addition of amines and of indoles to α,β-unsaturated ketones,[21] the condensation of indoles with carbonyl compounds,[22] the synthesis of aryloxazolines[23] and the acylation of alcohols, phenols, amines and thiols.[24] $ZrOCl_2$•$8H_2O$ 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[25,26] for development of useful synthetic methodology,[27] the reaction of *p*-chlorobenzaldehyde with 2-naphthol in the presence of a catalytic amount of $ZrOCl_2$•$8H_2O$ 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$_2$; b) X = 3-NO$_2$; c) X = H; d) X = 3-Cl; e) X = 4-CH$_3$; f) X = 2,4-Cl$_2$; g) X = 4-Br;
h) X = 2-Cl; i) X = 3-Br; j) X = 4-Cl; k) X = 3-CH$_3$; 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 $ZrOCl_2•8H_2O$ 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 $ZrOCl_2•8H_2O$ under thermal conditions.

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

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

[a] 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}H) and 125.77 (^{13}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 $ZrOCl_2.8H_2O$ (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}H NMR and ^{13}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. Sirkeeioglu, 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. Knignt and P. B. Little, *J. Chem. Soc. Perkin 1*, 1771 (**2001**). b) D. W. Knignt 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).

****