

## RESEARCH LETTER

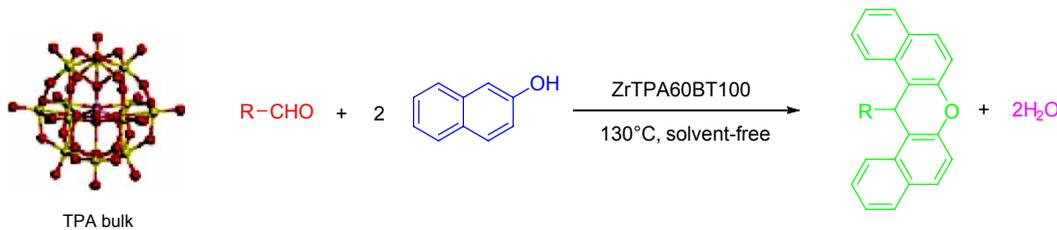
### Green catalytic synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes using recyclable mesoporous zirconia modified with tungstophosphoric acid

Toa S. Rivera, Mirta N. Blanco, Luis R. Pizzio and Gustavo P. Romanelli\*

*Departamento de Química, Facultad de Ciencias Exactas, Centro de Investigación y Desarrollo en Ciencias Aplicadas "Dr. Jorge J.J. Ronco" (CINDECA), UNLP-CCT La Plata CONICET, 47 N° 257, 1900 La Plata, Argentina*

*(Received 4 November 2011; final version received 23 December 2011)*

A simple and efficient procedure has been developed for the preparation of aryl-14H-dibenzo[a,j]xanthenes by a one-pot condensation of 2-naphthol and aryl aldehydes, in the presence of mesoporous zirconia modified with tungstophosphoric acid (ZrTPA60BT<sub>100</sub>), to be used as a heterogeneous catalyst in a solvent-free medium using conventional heating. The present approach offers the advantages of clean reaction, simple methodology, short reaction time, and high yield. The reaction work-up is very simple and the catalyst can be easily separated from the reaction mixture and reused several times in subsequent reactions without appreciable loss of the catalytic activity.



**Keywords:** mesoporous zirconia; heteropolyacids; 14-aryl-14H-dibenzo[a,j]xanthenes; heterogeneous catalysts; solvent-free synthesis

#### 1. Introduction

The preparation of organic compounds involving a greener process and under solvent-free conditions has been investigated worldwide due to stringent environmental and economic regulations. The implementation of several transformations in a single manipulation is highly compatible with the goals of Green Chemistry (1–3).

In the last two decades, inorganic solid-catalyzed organic transformations have gained much importance due to the proven advantage of heterogeneous catalysis, such as simplified product isolation, mild reaction conditions, high selectivities, easy catalyst recovery and reuse, and reduction in generation of waste byproducts (4–6).

Particularly, the catalysis by heteropolyacids (HPAs) and related compounds is a field of increasing importance worldwide. Numerous developments are being carried out in basic research as well as in fine

chemistry processes (7). Due to the strong acidic properties of solid HPAs, in the last decades, HPAs have found applications as useful and versatile acid catalysts for some acid-catalyzed reactions (8,9). They can be used in bulk or supported form in both homogeneous and heterogeneous systems. Furthermore, HPAs have several advantages, including high flexibility in modification of acid strength, environmental compatibility, nontoxicity, and ease of handling (10).

On the other hand, zirconia is an interesting material to be used as catalyst support due to its thermal stability in different atmospheres. Its acid properties can be modified by the addition of cationic or anionic substances, such as sulfate or tungstate (11–13). The addition of Keggin HPAs to modify them has been studied to a lesser extent (14–17).

The most common methods that can be used to obtain zirconia are the sol-gel method, the micellar

\*Corresponding author. Email: gpr@quimica.unlp.edu.ar



Table 1. Reaction between 2-naphthol and benzaldehyde under different conditions.

Entry	Catalizador	Temperature (°C)	Time (h)	Yield <sup>a</sup> (%)
1	Without catalyst	80	1.5	–
2		100	1.5	–
3		120	1.5	15
4		130	1.5	32
5		130	5	30
6	TPA bulk <sup>b</sup>	80	5	–
7		100	1	Traces
8		100	3	10
9		130	1	90
10	ZrTPA60B <sub>T100</sub> <sup>c</sup>	80	5	–
11		100	3	10
12		120	2	82
13		130	1	99
14		130 <sup>d</sup>	1	98
15		130 <sup>d</sup>	1	98
16		130 <sup>d</sup>	1	96

<sup>a</sup>The yields refer to the isolated product.

<sup>b</sup>TPA bulk = 50 mg.

<sup>c</sup>ZrTPA60B<sub>T100</sub> = 84 mg.

<sup>d</sup>First, second, and third reuse.

Finally, we studied the catalytic activity of the mesoporous zirconia modified with tungstophosphoric acid prepared in the present work. The ZrTPA60B<sub>T100</sub> was tested in the preparation of 1-phenyl-14*H*-dibenzo[*a,j*]xanthene. The experimental reaction conditions were 1.2 mmol of benzaldehyde, 2 mmol of 2-naphthol, 85 mg of supported catalyst, and solvent-free conditions. No reaction was observed at 80 °C and only a 10% yield of product was obtained at 100 °C for a reaction time of 3 h

Table 2. Synthesis of aryl-14*H*-dibenzo[*a,j*]xanthenes with ZrTPA60B<sub>T100</sub> as catalyst.<sup>a</sup>

Entry	Aromatic aldehyde	Time (h)	Yield <sup>b</sup> (%)
1	Benzaldehyde	1	99
2	4-Methylbenzaldehyde	1	94
3	4-Methoxybenzaldehyde	1	93
4	4-Fluorobenzaldehyde	2	98
5	4-Chlorobenzaldehyde	2	96
6	4-Bromobenzaldehyde	2	93
7	2-Chlorobenzaldehyde	2	89
8	2,4,6-Trimethoxybenzaldehyde	5	60
9	2-Naphthaldehyde	3	78
10	1-Naphthaldehyde	3	81

<sup>a</sup>Reaction conditions: aldehyde, 1.2 mmol; 2-naphthol, 2 mmol; catalyst: ZrTPA60B<sub>T100</sub>, 85 mg, 130 °C.

<sup>b</sup>The yields refer to the isolated product.

(Table 1, entries 10 and 11). The yield of 1-phenyl-14*H*-dibenzo[*a,j*]xanthene increased notably for a reaction time of 1 h at 130 °C. In this case, the yield was 99% (Table 1, entry 13), being noticeably more active than the bulk catalyst.

The reusability of the catalyst was checked by separating the mesoporous zirconia modified with tungstophosphoric acid catalyst from the reaction mixture by simple filtration, washing with toluene, and drying in a vacuum oven at room temperature for 4 h prior to reuse in subsequent reactions without significant loss in product yields (Table 1, entries 14, 15, and 16).

After optimization of the reaction conditions, we studied the generality of this condition to other substrates. Using this method, different substrates were reacted with 2-naphthol to produce the corresponding 14-aryl-14*H*-dibenzo[*a,j*]xanthenes at 130 °C in solvent-free conditions. The results are summarized in Table 2. Several aromatic aldehydes with different functional groups were subjected to the condensation reaction, and the desired products were synthesized in good to excellent yields. The substituted functional groups in the aromatic ring of the aldehyde affect the yield and the reaction time. In comparison with electron-withdrawing groups in the aldehyde, we found that the presence of electron-donating groups in the aldehyde decreased both the reaction rate and the yields of products (Table 2, entries 8, 9, and 10).

### 3. Experimental

All chemical reagents and solvents were obtained from Aldrich and were used without further purification. All products are known compounds and were identified by comparison of their physical and spectral data with those of the authentic samples. Melting points were measured on a Bioamerican Bs 448 apparatus and were uncorrected. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a Varian 200 MHz. The purity of the substances and the progress of the reaction were monitored by thin layer chromatography (TLC) on silica gel, and yields refer to isolated products.

#### 3.1. Preparation of catalyst

Zirconium propoxide (Aldrich, 26.6 g) was mixed with absolute ethanol (Merck, 336.1 g) and stirred for 10 min to obtain a homogeneous solution under N<sub>2</sub> at room temperature. Then 0.47 cm<sup>3</sup> of 0.28 M HCl aqueous solution was dropped slowly into the aforementioned mixture to catalyze the sol-gel reaction.

After 3 h, an appropriate amount of PEG–alcohol–water (1:5:1 weight ratio) solution was added to the hydrolyzed solution under vigorous stirring to act as template. The amount of added solution was fixed in order to obtain a template concentration of 10% by weight in the final material. A TPA solution (whose concentration was fixed in order to obtain TPA concentration of 60% w/w in the solid) was added together with the addition of PEG (sample ZrTPA60B).

The gel was kept in a beaker at room temperature up to dryness. The solid was ground into powder and extracted with distilled water for three periods of 8 h, in a system with continuous stirring, to remove PEG. Afterwards, the solids were calcined at 100 °C for 24 h.

### 3.2. Typical procedure for aryl-14H-dibenzo[a,j]xanthenes synthesis using ZrTPA60B<sub>T100</sub> catalyst

A mixture of the aldehyde (1.2 mmol), 2-naphthol (2 mmol), and ZrTPA60B<sub>T100</sub> (85 mg) was stirred at 130 °C for the appropriate time according to Table 1. Completion of the reaction was indicated by TLC. The reaction mixture was cooled to 25 °C, toluene (5 cm<sup>3</sup>) was added, and then the mixture was stirred for 15 min and filtered to separate the catalyst, which was subsequently washed twice with toluene (3 cm<sup>3</sup>). The combined toluene extracts were washed twice with water (5 cm<sup>3</sup>), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated in vacuo. The solid obtained was recrystallized from ethyl alcohol to afford the pure 14-aryl-14H-dibenzo[a,j]xanthenes derivatives. After the reaction, the catalyst was filtered, washed thoroughly with toluene, dried in a vacuum oven (room temperature, 4 h) and reused for the next reaction, following the procedure described earlier.

### 3.3. Representative spectral <sup>1</sup>H-NMR and <sup>13</sup>C-NMR data

*14-(4-Methylphenyl)-14H-dibenzo[a,j]xanthenes* (Table 1, entry 2): Mp: 237–239 °C. <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>): δ 2.15 (s, 3H), 6.37 (s, 1H), 6.92 (d, *J* = 9.5 Hz, 2H), 7.30–7.78 (m, 12H), 8.33 (d, *J* = 9.4 Hz, 2H). <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>): δ 19.2, 35.2, 115.8, 116.3, 121.3, 122.8, 125.3, 126.5, 127.6, 129.3, 129.3, 129.4, 129.5, 134.0, 140.8, 146.6.

*14-(4-Methoxyphenyl)-14H-dibenzo[a,j]xanthenes* (Table 1, entry 3): 211–214 °C. <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>): δ 3.55 (s, 3H), 6.42 (s, 2H), 6.64 (d, *J* = 9.6 Hz, 2H), 7.30–7.82 (m, 12H), 8.35 (d, *J* = 9.6 Hz, 2H). <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>): δ 36.5, 53.1, 114.3, 117.4, 118.5, 123.6, 124.2, 127.3, 128.1, 129.2, 129.5, 131.5, 133.8, 137.4, 149.1, 158.1.

*14-(4-Chlorophenyl)-14H-dibenzo[a,j]xanthenes* (Table 1, entry 5): 288–290 °C. <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>): δ 6.44 (s, 1H), 7.08–8.32 (m, 16H). <sup>13</sup>C-NMR (50 MHz, CDCl<sub>3</sub>): 37.4, 116.8, 118.2, 122.5, 125.4, 126.9, 128.7, 129.0, 129.5, 129.6, 131.1, 131.3, 132.0, 143.5, 148.7.

## 4. Conclusion

In conclusion, ZrTPA60B<sub>T100</sub> as a noncorrosive, environmentally friendly and stable heterogeneous material has been proved to be a very efficient catalyst for the synthesis of dibenzoxanthene derivatives. A convenient and green process for the synthesis of aryl-14H-dibenzo[a,j]xanthenes by condensation of various aromatic aldehydes with 2-naphthol using ZrTPA60B<sub>T100</sub> as a heterogeneous acid catalyst in a solvent-free medium using conventional heating at 130 °C has been developed. In addition, short reaction times, excellent yields, a straightforward procedure, and relative nontoxicity of the catalyst are other noteworthy advantages of the present method. Finally, this solid acid catalyst can be recovered and reused at least four times with negligible loss in its activity. Further applications of ZrTPA60B<sub>T100</sub> in green organic transformations are currently in progress in our laboratory.

## Acknowledgements

The authors thank Agencia Nacional de Promoción Científica y Tecnológica, CONICET, and Universidad Nacional de La Plata for financial support, and L. Soto, L. Osiglio, D. Peña, and N. Firpo for their experimental collaboration in the experimental measurements.

## References

- (1) Kumar, R.; Nandi, G.; Verma, R.; Singh, M. *Tetrahedron Lett.* **2010**, *51*, 442–445.
- (2) Rahmati, A. *Chinese Chem. Lett.* **2010**, *21*, 761–764.
- (3) Kumar, R.; Nandi, G.; Verma, R.; Singh, M. *Tetrahedron Lett.* **2010**, *51*, 442–445.
- (4) Clark, J. *Acc. Chem. Res.* **2002**, *35*, 791–797.
- (5) Okuhara, T. *Chem. Rev.* **2002**, *102*, 3641–3666.
- (6) Wilson, K.; Clark, J.H. *Pure Appl. Chem.* **2000**, *72*, 1313–1319.
- (7) Misono, M.; Nojiri, N. *Appl. Catal. A: Gen.* **1990**, *64*, 1–30.
- (8) Amini, M.; Seyyedhamzeh, M.; Bazgir, A. *Appl. Catal. A: Gen.* **2007**, *323*, 242–245.
- (9) Kozhevnikov, I. *J. Mol. Catal. A: Chem.* **2007**, *262*, 86–92.
- (10) Kozhevnikov, I. *Chem. Rev.* **1998**, *98*, 171–198.
- (11) Yadav, G.; Nair, J. *Micropor. Mesopor. Mater.* **1999**, *33*, 1–48.
- (12) Boyse, R.; Ko, E. *J. Catal.* **1997**, *171*, 191–207.

- (13) Zhao, B.; Xu, X.; Ma, H.; Sun, D.; Gao, J. *Catal. Lett.* **1997**, *45*, 237–244.
- (14) Devassy, B.; Shanbhag, G.; Halligudi, S. *J. Mol. Catal. A: Chem.* **2006**, *247*, 162–170.
- (15) Mallik, S.; Dash, S.; Parida, K.; Mohapatra, B. *J. Colloid Interf. Sci.* **2006**, *300*, 237–243.
- (16) Qu, X.; Guo, Y.; Hu, Ch. *J. Mol. Catal. A: Chem.* **2007**, *262*, 128–135.
- (17) Pizzio, L.; Vázquez, P.; Cáceres, C.; Blanco, M. *Catal. Lett.* **2001**, *77*, 233–239.
- (18) Fernández-García, M.; Martínez-Arias, A.; Hanson, J.; Rodríguez, J. *Chem. Rev.* **2004**, *104*, 4063–4104.
- (19) Madhav, J.; Reddy, Y.; Reddy, P.; Reddy, M.; Kuarm, S.; Crooks, P.; Rajitha, B. *J. Mol. Catal. A: Chem.* **2009**, *304*, 85–87.
- (20) Chibale, K.; Visser, M.; Schalkwyk, D.; Smith, P.; Saravanamuthu, A.; Fairlamb, A. *Tetrahedron* **2003**, *59*, 2289–2296.
- (21) El-Brashy, A.; Metwally, M.; El-Sepai, F. *Farmaco* **2004**, *59*, 809–817.
- (22) Jamison, J.; Krabill, K.; Hatwalkar, A. *Cell. Biol. Int. Resp.* **1990**, *14*, 1075–1084.
- (23) Lewis, J.; Readhead, M. *J. Med. Chem.* **1970**, *13*, 525.
- (24) Ion, R. *Prog. Catal.* **1997**, *2*, 55.
- (25) Saint-Ruf, G.; De, A.; Hieu, H. *Bull. Chim. Ther.* **1972**, *7*, 83–86.
- (26) Banerjee, A.; Mukherjee, A. *Stain Technol.* **1981**, *56*, 83–85.
- (27) Knight, C.; Stephenes, T. *Biochem. J.* **1989**, *258*, 683–689.
- (28) Callan, J.; De Silva, P.; Magri, D. *Tetrahedron* **2005**, *61*, 8551.
- (29) Sirkecioglu, O.; Tulinli, N.; Akar, A. *J. Chem. Res. (S)* **1995**, 502–503.
- (30) Mirjalili, B.; Bamoniri, A.; Akbari, A. *Chim. Chem. Lett.* **2011**, *22*, 45–48.
- (31) Sharma, R.; Baruah, J. *Dyes Pigments* **2005**, *64*, 91.
- (32) Khosropour, A.; Khodaei, M.; Moghannian, H. *Synlett* **2005**, 995.
- (33) Das, B.; Ravikanth, B.; Ramu, R.; Laxminarayana, K.; Rao, B. *J. Mol. Catal. A: Chem.* **2006**, *255*, 74.
- (34) Ko, S.; Yao, C. *Tetrahedron Lett.* **2006**, *47*, 8827.
- (35) Zarei, A.; Hajipour, A.; Khazdooz, L. *Dyes Pigments* **2010**, *85*, 133–138.
- (36) Mozhdesh, S.; Peiman, M.; Bazgir, A. *Dyes Pigments* **2008**, *76*, 836.
- (37) Shakibaei, G.; Mirzaei, P.; Bazgir, A. *Appl. Catal. A: Gen.* **2007**, *325*, 188–192.
- (38) Kanteravi, S.; Chary, M.; Das, A.; Vuppalapati, S.; Lingaiah, N. *Catal. Commun.* **2008**, *9*, 1575–1578.
- (39) Nagarapu, L.; Kantevari, S.; Mahankhali, V.; Apuri, S. *Catal. Commun.* **2007**, *8*, 1173–1177.
- (40) Amini, M.; Seyyedhamzeh, M.; Bazgir, A. *Appl. Catal. A: Gen.* **2007**, *323*, 242–245.
- (41) Kumar, R.; Nandi, G.; Verna, R.; Singh, M. *Tetrahedron Lett.* **2010**, *51*, 442–445.
- (42) Romanelli, G.; Bennardi, D.; Ruiz, D.; Baronetti, G.; Thomas, H.; Autino, J. *Tetrahedron Lett.* **2004**, *45*, 8935–8939.
- (43) Romanelli, G.; Sathicq, A.; Autino, J.; Thomas, H.; Baronetti, G. *Synth. Commun.* **2007**, *37* (22), 3907–3916.
- (44) Romanelli, G.; Autino, J.; Vázquez, P.; Pizzio, L.; Blanco, M.; Cáceres, C. *Appl. Catal. A: Gen.* **2009**, *352*, 208–213.
- (45) Bennardi, D.; Romanelli, G.; Autino, J.; Pizzio, L.; Vázquez, P.; Cáceres, C.; Blanco, M. *React. Kinet. Mechanism Catal.* **2010**, *100*, 165–174.