



Synthesis of Tetrahydrobenzo[*a*]xanthene-11-one Derivatives Using ZrO₂-SO₃H as Highly Efficient Recyclable Nano-catalyst

Ahmad Nakhaei*, Sepideh Yadegarian

Young Researchers and Elite Club, Mashhad Branch, Islamic Azad University, Mashhad, Iran

(Received 12 Dec. 2016; Final version received 19 Mar. 2017)

Abstract

The catalytic effect of Zirconia Sulfuric Acid (ZrSA) nanoparticle which is synthesized from the reaction of ZrO₂ with chlorosulfonic acid has been investigated in the synthesis of tetrahydrobenzo[*a*]xanthene-11-ones by one-pot three-component reaction of β -naphthol, aromatic aldehydes, and dimedone. Different reaction conditions were studied in the presence of ZrSA nanoparticle as catalyst. The results showed that ZrSA exhibited high catalytic activity towards the synthesis of tetrahydrobenzo[*a*]xanthene-11-ones, with the desired products being formed in high yields. Furthermore, the catalyst was recyclable and could be reused at least three times without any discernible loss in its catalytic activity. Overall, this new catalytic method for the synthesis of tetrahydrobenzo[*a*]xanthene-11-ones provides rapid access to the desired compounds under solvent-free conditions at 110 °C following a simple work-up procedure, and avoids the use of harmful organic solvents. This method therefore represents a significant improvement over the methods currently available for the synthesis of tetrahydrobenzo[*a*]xanthene-11-ones.

Keywords: Solid acid Nano-catalyst, Reusability, Zirconia sulfuric acid (ZrSA), Tetrahydrobenzo[*a*]xanthene-11-ones, Solvent-free.

*Corresponding author: Ahmad Nakhaei, Young Researchers and Elite Club, Mashhad Branch, Islamic Azad University, Mashhad, Iran. E-mail: nakhaei_a@mshdiau.ac.ir, nakhaei_a@yahoo.com.

Introduction

Acid-catalysts are one of the most frequently applied processes in chemical industry, which has been a major area of research interest [1]. Commonly, liquid inorganic acids including H_2SO_4 , HCl and H_3PO_4 are part of the homogeneous acid catalysts. Despite their application in the wide production of industrial chemicals, many disadvantages such as high toxicity, corrosive nature, hazards in handling and difficult separation from the products make them not so useful. Furthermore, the synthesis using homogeneous catalysts have major problem of catalyst recovery and reuse.

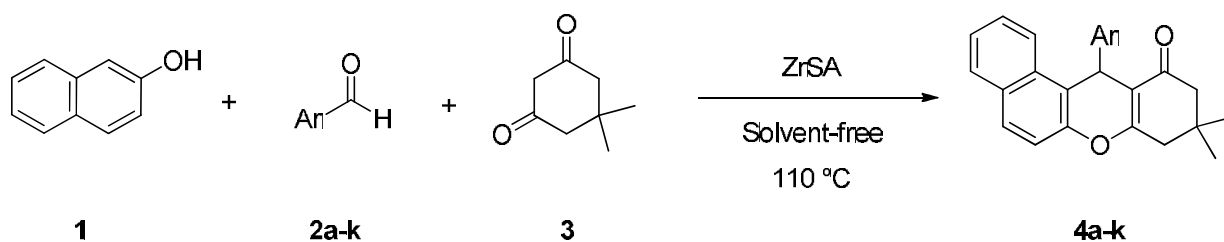
These difficulties are not in the range of green chemistry. According to these disadvantages, in order to improve drawbacks of these catalysts, replacement of them by novel, nontoxic, eco-friendly, recyclable heterogeneous catalysts with improved efficiency have been the important topics of researchers during the last decades. Heterogeneous catalysts show important role in many aspects of environmental and economic in many industrial processes. They presented some excellence including great reactivity, operational simplicity, low toxicity, non-corrosive nature and the potential of the recyclability. Furthermore, most of the heterogeneous catalysts show better product selectivity, so that by-product can be easily separated [2]. One of the important routes for developing novel heterogeneous catalysts is immobilizing of homogenous precursors on a solid support [3].

The metal oxide nanoparticles such as TiO_2 , MgO , Al_2O_3 , and ZnO are reported as useful heterogeneous catalyst agents in the synthesis of organic compounds [4, 5]. Zirconia (ZrO_2) is one of the most important metal oxide nanoparticles with high surface area, mechanical strength and thermal stability which have widely application in chemical industry especially as catalyst [6]. Benzoxanthenes are an important class of oxygen containing organic compounds with low molecular weight that synthesized *via* MCR includes the condensation of β -naphthol, aromatic aldehydes, and dimedone, as primary reagents [7].

Some literature demonstrated pharmacological and therapeutic effects of xanthene structure such as antibacterial [8], anti-inflammatory [9], and antiviral [10]. Besides, they have been used as antagonists for paralyzing the action of zoxazolamine [11] and in photodynamic therapy [12]. Moreover, they also find application in industries such as dyes [13], pH-sensitive fluorescent materials to monitor changes in intracellular pH [14] and in laser technologies [15].

Many synthetic protocols were developed to accelerate the rate of benzoxanthenes synthesis and to improve the yield. These compounds have been synthesized in the presence of various Lewis and Brønsted acid catalyst have been utilized in the construction of the benzoxanthenes skeleton [16–31]. Major drawbacks of these procedures include expensive reagents, use of large amounts of toxic organic solvents, prolonged heating and side reactions. All of these disadvantages make further improvement of the synthesis of such molecules essential. Therefore, the development of a new greener and more convenient method using a new catalyst with high catalytic activity for the synthesis of benzoxanthenes is highly desirable.

As part of our research program on the development of convenient methods using reusable catalysts for the synthesis of organic compounds [32–35]. We report here the results of our investigation on the application of Zirconia Sulfuric Acid (ZrSA) nanoparticle as heterogeneous catalysts in the synthesis of tetrahydrobenzo[*a*]xanthene-11-ones (Scheme 1).



Scheme 1. ZrSA catalyzed synthesis of tetrahydrobenzo[*a*]xanthene-11-ones.

Experimental

Chemicals and apparatus

All chemicals were available commercially and used without additional purification. Zirconium oxide (ZrO_2) was purchased from Aldrich. The ZrSA catalyst was synthesized according to the literature [36]. Melting points were recorded using a Stuart SMP3 melting point apparatus. The FT-IR spectra of the products were obtained with KBr disks, using a Tensor 27 Bruker spectrophotometer. The ^1H NMR spectra were recorded using Bruker (400 MHz) spectrometers.

*General experimental procedure for the synthesis of tetrahydrobenzo[*a*]xanthene-11-ones 4a-4k catalyzed by ZrSA*

A mixture of 4-chlorobenzaldehydes (1 mmol), β -naphthol (1 mmol), and dimedone (1 mmol), and ZrSA (0.1 g) as catalyst was heated in the oil bath at 110 °C for 13–20 min. The reaction was monitored by TLC. Upon completion of the transformation, hot ethanol was added and the catalyst filtered through sintered glass Büchner funnel under hot conditions. The catalyst was washed with a small portion of hot ethanol. After cooling, the combined filtrate was allowed to stand at room temperature. The precipitated solid was collected by filtration, and recrystallized from ethanol to give compounds 4a-4k in high yields.

9,9-Dimethyl-12-phenyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4a)

Yield: 93%, 14 min; Mp 151-152 °C (EtOH) [lit. [19] 149–151 °C (EtOH)]; ¹H NMR (400 MHz, CDCl₃): δ 0.99 (s, 3H, CH₃), 1.15 (s, 3H, CH₃), 2.31 (AB_q, $\Delta\nu = 27.6$ Hz, $J_{AB} = 16.4$ Hz, 2H, CH₂), 2.61 (s, 2H, CH₂), 5.74 (s, 1H, CH), 7.09 (tt, $J = 7.6, 2.0$ Hz, 1H, arom-H), 7.20 (t, $J = 7.6$ Hz, 2H, arom-H), 7.35–7.50 (m, 5H, arom-H), 7.80 (d, $J = 8.8$ Hz, 2H, arom-H), 8.02 (d, $J = 8.4$ Hz, 1H, arom-H); IR (KBr disc): ν 2962, 1595, 1492, 1447, 1374, 1299, 1250, 1166, 870 cm⁻¹.

9,9-Dimethyl-12-(3-nitrophenyl)-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4b)

Yield: 91%, 15 min; Mp 166-168 °C (EtOH) [lit. [19] 168–172 °C (EtOH)]; ¹H NMR (400 MHz, CDCl₃): δ 0.98 (s, 3H, CH₃), 1.16 (s, 3H, CH₃), 2.31 (AB_q, $\Delta\nu = 35.2$ Hz, $J_{AB} = 16.4$ Hz, 2H, CH₂), 2.64 (s, 2H, CH₂), 5.84 (s, 1H, CH), 7.38-7.50 (m, 4H, arom-H), 7.82–7.92 (m, 4H, arom-H), 7.96 (dd, $J = 8.0, 1.2$ Hz, 1H, arom-H), 8.14 (s, 1H, arom-H); IR (KBr disc): ν 3089, 2961, 2870, 1597, 1527, 1378, 1342, 1251, 1044, 894 cm⁻¹.

9,9-Dimethyl-12-(4-nitrophenyl)-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4c)

Yield: 95%, 13 min; Mp 180-181 °C (EtOH) [lit. [19] 178–181 °C (EtOH)]; ¹H NMR (400 MHz, CDCl₃): δ 0.98 (s, 3H, CH₃), 1.17 (s, 3H, CH₃), 2.32 (AB_q, $\Delta\nu = 36.4$ Hz, $J_{AB} = 16.4$ Hz, 2H, CH₂), 2.63 (AB_q, $\Delta\nu = 20.0$ Hz, $J_{AB} = 18.0$ Hz, 2H, CH₂), 5.85 (s, 1H, CH), 7.38–7.50 (m, 3H, arom-H), 7.55 (d, $J = 8.4$ Hz, 2H, arom-H), 7.84–7.88 (m, 3H, arom-H), 8.07 (d, $J = 8.4$ Hz, 2H, arom-H); IR (KBr disc): ν 3074, 2956, 1646, 1619, 1595, 1516, 1376, 1345, 1223, 1183, 850 cm⁻¹.

9,9-Dimethyl-12-(4-methylphenyl)-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4d)

Yield: 96%, 16 min; Mp 176-178 °C (EtOH) [lit. [23] 175–176 °C (EtOH)]; IR (KBr disc): ν 3080, 2963, 2921, 1632, 1497, 1478, 1371, 1225, 1186, 1154, 1011, 842, 811, 748 cm^{-1} .

12-(4-methoxyphenyl)-9,9-Dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4e)

Yield: 96%, 18 min; Mp 205-207 °C (EtOH) [lit. [23] 207–208 °C (Column chromatography over silica gel using ethyl acetate/cyclohexane)]; IR (KBr disc): ν 3091, 2966, 2867, 1619, 1589, 1485, 1371, 1225, 1184, 1166, 1017, 835, 812, 753 cm^{-1} .

12-(4-Chlorophenyl)-9,9-Dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4f)

Yield: 94%, 15 min; Mp 190-192 °C (EtOH) [lit. [23] 188–189 °C (Column chromatography over silica gel using ethyl acetate/cyclohexane)]; ^1H NMR (400 MHz, CDCl_3): δ 0.99 (s, 3H, CH_3), 1.15 (s, 3H, CH_3), 2.31 (AB_q, $\Delta\nu = 28.8$ Hz, $J_{AB} = 16.4$ Hz, 2H, CH_2), 2.60 (s, 2H, CH_2), 5.72 (s, 1H, CH), 7.16 (d, $J = 8.0$ Hz, 2H, arom-H), 7.28–7.50 (m, 5H, arom-H), 7.82 (t, $J = 8.0$ Hz, 2H, arom-H), 7.93 (d, $J = 8.0$ Hz, 1H, arom-H); IR (KBr disc): ν 3079, 2953, 2870, 1650, 1597, 1488, 1371, 1225, 1184, 1166, 1017, 835, 812, 753 cm^{-1} .

12-(2-Chlorophenyl)-9,9-Dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4g)

Yield: 89%, 20 min; Mp 178-180 °C (EtOH) [lit. [25] 179–181 °C (Column chromatography over silica gel using ethyl acetate/light petrol)]; ^1H NMR (400 MHz, CDCl_3): δ 1.03 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 2.30 (AB_q, $\Delta\nu = 36.6$ Hz, $J_{AB} = 16.0$ Hz, 2H, CH_2), 2.64 (s, 2H, CH_2), 6.03 (s, 1H, CH), 7.00–7.12 (m, 2H, arom-H), 7.28–7.38 (m, 3H, arom-H), 7.41 (t, $J = 7.2$ Hz, 1H, arom-H), 7.51 (t, $J = 7.6$ Hz, 1H, arom-H), 7.79 (t, $J = 8.4$ Hz, 2H, arom-H), 8.26 (d, $J = 8.8$ Hz, 1H, arom-H); IR (KBr disc): ν 3059, 2946, 1651, 1619, 1597, 1471, 1370, 1226, 1143, 1100, 812, 743 cm^{-1} .

12-(4-Bromophenyl)-9,9-Dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4h)

Yield: 92%, 19 min; Mp 185-187 °C (EtOH) [lit. [26] 187–189 °C (EtOH)]; IR (KBr disc): ν 3052, 2965, 1620, 1594, 1472, 1429, 1378, 1283, 1225, 1177, 805, 743 cm^{-1} .

12-(3-Bromophenyl)-9,9-Dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4i)

Yield: 90%, 17 min; Mp 166-168 °C (EtOH) [lit. [26] 170–171 °C (EtOH)]; ^1H NMR (400 MHz, CDCl_3): δ 1.01 (s, 3H, CH_3), 1.15 (s, 3H, CH_3), 2.32 (AB_q , $\Delta\nu = 22.6$ Hz, $J_{AB} = 16.0$ Hz, 2H, CH_2), 2.61 (AB_q , $\Delta\nu = 20.6$ Hz, $J_{AB} = 17.6$ Hz, 2H, CH_2), 5.71 (s, 1H, CH), 7.08 (t, $J = 8.0$ Hz, 1H, arom-H), 7.20–7.25 (m, 1H, arom-H), 7.35–7.52 (m, 5H, arom-H), 7.80–7.85 (m, 2H, arom-H), 7.95 (d, $J = 8.4$ Hz, 1H, arom-H); IR (KBr disc): ν 2955, 1650, 1594, 1471, 1375, 1220, 1167, 875, 807 cm^{-1} .

12-(4-Fluorophenyl)-9,9-Dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4j)

Yield: 95%, 15 min; Mp 186-188 °C (EtOH) [lit. [26] 185–186 °C (EtOH)]; ^1H NMR (400 MHz, CDCl_3): δ 0.99 (s, 3H, CH_3), 1.15 (s, 3H, CH_3), 2.31 (AB_q , $\Delta\nu = 28.4$ Hz, $J_{AB} = 16.0$ Hz, 2H, CH_2), 2.60 (s, 2H, CH_2), 5.72 (s, 1H, CH), 6.88 (t, $J = 8.8$ Hz, 2H, arom-H), 7.28–7.50 (m, 5H, arom-H), 7.82 (t, $J = 8.8$ Hz, 2H, arom-H), 7.95 (d, $J = 8.0$ Hz, 1H, arom-H); IR (KBr disc): ν 2956, 1650, 1595, 1507, 1466, 1375, 1227, 1185, 1143, 840, 815, 745 cm^{-1} .

9,9-Dimethyl-12-(thiophen-2-yl)-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4k)

Yield: 96%, 14 min; Mp 181-183 °C (EtOH) [lit. [26] 177–179 °C (EtOH)]; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 0.99 (s, 3H, CH_3), 1.09 (s, 3H, CH_3), 2.23 (d, $J = 16.0$ Hz, 1H, one proton of diastereotopic protons in CH_2), 2.40 (d, $J = 16.0$ Hz, 1H, one proton of diastereotopic protons in CH_2), 2.65 (AB_q , $\Delta\nu = 43.0$ Hz, $J_{AB} = 16.4$ Hz, 2H, CH_2), 5.94 (s, 1H, CH), 6.79 (dd, $J = 5.2, 3.6$ Hz, 1H, arom-H), 6.85 (d, $J = 2.8$ Hz, 1H, arom-H), 7.22 (dd, $J = 5.0, 1.2$ Hz, 1H, arom-H), 7.44–7.51 (m, 2H, arom-H), 7.57 (t, $J = 8.8$ Hz, 1H, arom-H), 7.96 (d, $J = 8.8$ Hz, 2H, arom-H), 8.11 (d, $J = 8.4$ Hz, 1H, arom-H); IR (KBr disc): ν 3052, 2962, 1651, 1594, 1376, 1358, 1223, 1177, 1147, 840, 700 cm^{-1} .

Results and discussion

Characterization of the catalyst

For our investigations, the catalyst $\text{ZrO}_2\text{--SO}_3\text{H}$ (ZrSA) was prepared according to the literature procedure [36]. The ZrSA catalyst was characterized by FT-IR, and pH analysis. The FT-IR spectrum of the nano- ZrO_2 and $\text{ZrO}_2\text{--SO}_3\text{H}$ are shown in Figure 2(1) and (2), respectively. In Figure 2(1), the characteristic vibrational bands of the Zr–O bond at 576 and 752 cm^{-1} , as well band belonging to the Zr–OH group at 1627 cm^{-1} . The FT-IR spectrum of the catalyst also

contained absorbance band at 3421 cm^{-1} , which indicated the presence of water. These observations proved nano-ZrO₂ structures and are consistent with the previously reported evidences [36, 37]. The FT-IR spectrum of the ZrSA catalyst prepared in the current study (Figure 2(2)) revealed new bonds at 820-890 and 1060–1180 cm^{-1} which are related to the O=S=O asymmetric and symmetric stretching vibration and S–O stretching vibration of the sulfonic groups (-SO₃H), respectively. The appeared broad band around 2700–3600 cm^{-1} related to the OH stretching absorption of the SO₃H group. All these specifications acknowledge nano-ZrO₂ structure that has functionalized with sulfonic acid groups. The density of the SO₃H groups was measured using NaOH (0.1 N) as titrant by acid-base potentiometric titration. The amount of SO₃H in the catalyst was 2.45 mmol/g.

Evaluation of catalytic activity of ZrSA in the synthesis of tetrahydrobenzo[a]xanthene-11-ones

In the effort to develop an efficient and environmentally benign method for synthesis of tetrahydrobenzo[a]xanthene-11-ones we initiated our studies by adding a catalytic amount of ZrSA to a mixture of β -naphthol (1 mmol), 4-chlorobenzaldehyde (1 mmol), and dimedone (1 mmol), as model reaction in different solvents such as EtOH, H₂O, MeOH, CH₃CN, CH₂Cl₂, CH₃CO₂Et, and also under solvent-free conditions (Table 1). We were pleased to see that the reaction was efficiently catalyzed by ZrSA under solvent-free conditions at elevated temperature leading to a high yield of the product 4f. The reaction conditions were then optimized by conducting the reaction at different temperatures and using different amounts of catalyst. The results are summarized in Table 1. Low yield of the product was obtained in the absence of the catalyst at 110 °C after 120 min (entry 1) indicating that the catalyst is necessary for the reaction. The best result was obtained when the reaction was run at 110 °C in the presence of 0.1 g ZrSA under solvent-free conditions (entry 15).

Thereafter, the applicability of the method was evaluated for the synthesis of other tetrahydrobenzo[a]xanthene-11-ones using a wide range of substituted aromatic aldehydes. The substituents in the aromatic ring of aldehydes or use of heteroaromatic aldehydes have no significant effect on the time of the reaction and yield of the products. Under the same conditions, however, no reaction occurred when aliphatic aldehydes were used. ZrSA nanoparticle efficiently catalyzed the reactions, giving the desired products 4a-k in high yields over relatively short reaction times. Easy separation of obtained products from the catalyst makes this method useful for the synthesis of tetrahydrobenzo[a]xanthene-11-ones.

Table 1. Synthesis of compound 4f in the presence of the ZrSA nanoparticle as catalysts under different reaction conditions.

Entry	Catalyst amount (g)	Solvent	T (°C)	Time (min)	Yield* (%)
1	-----	-----	110	120	19
2	0.02	-----	90	80	45
3	0.02	-----	110	75	51
4	0.02	-----	130	75	48
5	0.04	-----	90	70	49
6	0.04	-----	110	68	55
7	0.04	-----	130	70	56
8	0.06	-----	90	56	63
9	0.06	-----	110	45	69
10	0.06	-----	130	55	69
11	0.08	-----	90	37	77
12	0.08	-----	110	32	85
13	0.08	-----	130	35	86
14	0.10	-----	90	20	88
15	0.10	-----	110	15	94
16	0.10	-----	130	18	93
17	0.12	-----	90	15	89
18	0.12	-----	110	15	93
19	0.12	-----	130	17	93
20	0.10	EtOH	Reflux	120	52
21	0.10	MeOH	Reflux	120	47
22	0.10	CH ₂ Cl ₂	Reflux	120	35
23	0.10	CH ₃ CN	Reflux	120	42
24	0.10	H ₂ O	Reflux	120	60
25	0.10	CH ₃ CO ₂ Et	Reflux	120	55

Reaction conditions: β -naphthol 1 (1 mmol), 4-chlorobenzaldehyde 2f (1 mmol), and dimedone 3 (1 mmol).

*Isolated yields.

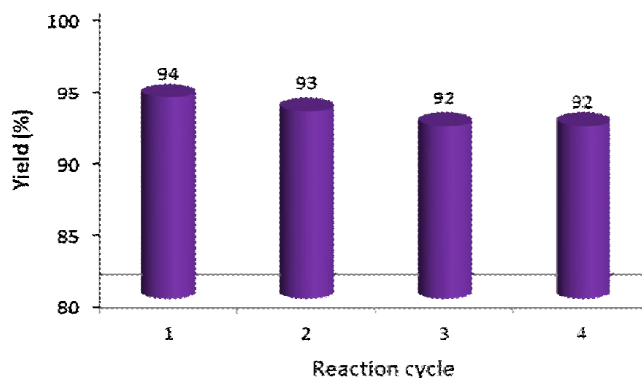
Purity checks with melting points, TLC, and the selected ¹H NMR spectroscopic data reveal that only one product is formed in all cases and no undesirable side-products are observed. All of the products were characterized by IR spectroscopy and a comparison of their melting points with those of the authentic samples. Some of the products were also confirmed by ¹H NMR spectroscopy.

We compared the results we obtained using ZrSA as catalyst with previously reported results for the synthesis of tetrahydrobenzo[*a*]xanthene-11-ones in the presence of various catalysts (Table 2). Our reaction conditions showed shorter reaction times than all the other conditions and gave high yields of the desired products.

Table 2. Comparison of the efficiencies of different catalysts for the synthesis of tetrahydrobenzo[*a*]xanthene-11-ones.

Catalyst	Conditions			Time (min)	Yield (%)	[Ref.]
	Solvent	T (°C)	Other			
PEG-400	---	120	---	330-450	79-90	[16]
HY zeolite	---	80	---	60-240	70-95	[17]
I ₂	AcOH	reflux	---	150-180	70-89	[18]
SO ₃ H-functionalized ionic liquids	---	120	---	55-95	75-95	[19]
Guanidine hydrochloride	---	80	---	25-60	88-93	[20]
Rice husk	---	90	---	30-60	93-98	[21]
ρ -TSA	---	120	---	35-45	80-92	[22]
Cyanuric chloride	---	80	---	30-70	84-93	[23]
HClO ₄ /SiO ₂	---	80	---	48-90	86-95	[24]
CAN	CH ₂ Cl ₂ /EtOH	26	ultrasound	120-144	82-87	[25]
Ce(SO ₄) ₂ .4H ₂ O	---	120	---	8-30	85-97	[26]
NaHSO ₄ -SiO ₂	ClCH ₂ CH ₂ Cl	reflux	---	280-420	69-89	[27]
InCl ₃	---	120	---	30-75	63-88	[28]
H ₃ PW ₁₂ O ₄₀	---	60	---	40-90	81-94	[29]
Sulfamic acid	---	120	---	115-136	79-84	[30]
Sr(OTf) ₂	ClCH ₂ CH ₂ Cl	80	---	300-420	70-88	[31]
ZrSA	---	110	---	13-20	89-96	This work

We also used the model reaction under optimized reaction conditions to evaluate the reusability of the ZrSA catalyst. After completion of the reaction, the catalyst was recovered as described in the experimental section. The separated catalyst was washed with hot ethanol and subsequently dried at 50 °C under vacuum for 1 h before being reused in a similar reaction. We found that the catalyst could be used at least four times with only a slight reduction in activity (Figure 1). Furthermore, the FT-IR spectra of the recovered catalysts (Figure 2(3)–(5)) were almost identical to the spectrum of the fresh catalyst (Figure 2(2)), indicating that the structure of the catalyst was unchanged by the reaction.

**Figure 1.** Effect of recycling on catalytic performance of ZrSA in the synthesis of 4f in model reaction.

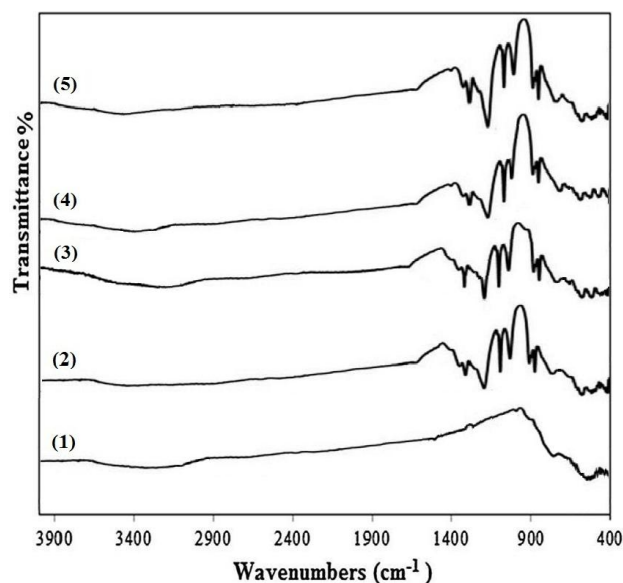
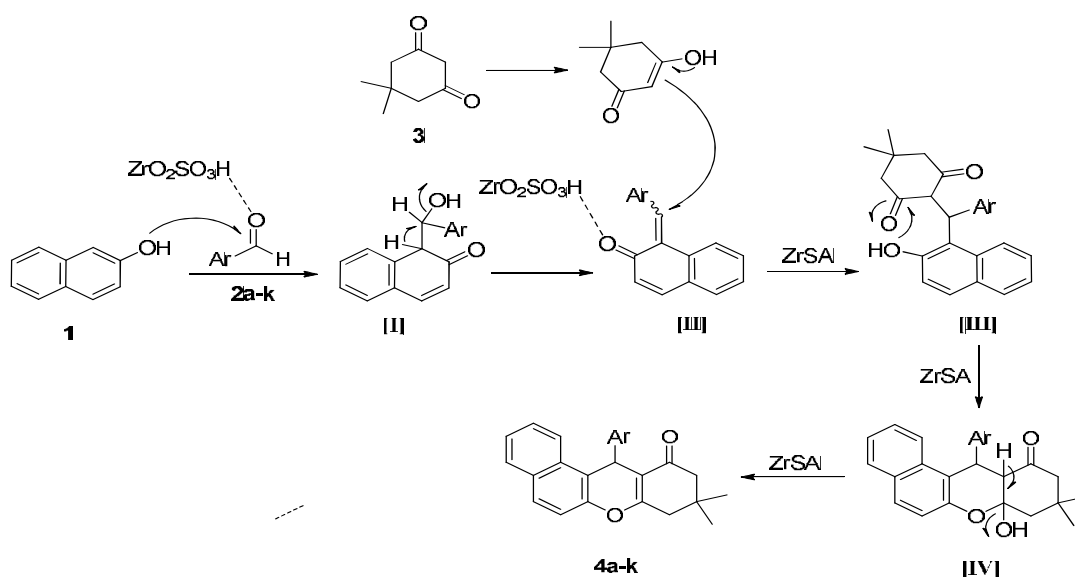


Figure 2. FT-IR spectra of ZrO_2 (1), fresh catalyst ZrSA ((2), first run), and recovered catalysts (3-5).

Plausible mechanism for this reaction may proceed as depicted in Scheme 2. ZrSA could act as Brønsted acid and therefore promote the necessary reactions. The catalyst would play a significant role in increasing the electrophilic character of the electrophiles in the reaction. According to this mechanism, the ZrSA catalyst would facilitate the formation of intermediates I, II, III and IV. Under these conditions, however, attempts to isolate the proposed intermediates failed even after careful monitoring of the reactions.



Scheme 2. Plausible mechanism for the ZrSA-catalyzed formation of tetrahydrobenzo[*a*]xanthene-11-ones.

Conclusion

In summary, we showed that Zirconia Sulfuric Acid (ZrSA) catalyzed the synthesis of tetrahydrobenzo[*a*]xanthene-11-ones by one-pot, three-component reaction of aromatic aldehydes, β -naphthol, and dimedone, at 110 °C under solvent-free conditions. The method was relatively fast and high yielding, and the work-up was easy. The catalyst can be recycled after simple handling, and used at least four times without any substantial reduction in its catalytic activity. The procedure is also advantageous in the sense that it is a fast reaction under solvent-free conditions and therefore operates under environmentally friendly conditions.

Acknowledgements

This project is dedicated to Kiyana Nakhaei, Zohreh Nakhaei, Hamid-reza Nakhaei, Kiyumars Nakhaei, Danyal Nakhaei, and Mahmood-reza Nakhaei

References

- [1] A. Davoodnia, M.M. Heravi, L. Rezaei-Daghigh, N. Tavakoli-Hoseini, *Monatsh. Chem.*, 140, 1499 (2009).
- [2] B.M. Bhanage, S.I. Fujita, Y. Ikushima, M. Arai, *Appl. Catal. A Gen.*, 219, 259 (2001).
- [3] B. Jahanbin, A. Davoodnia, H. Behmadi, N. Tavakoli-Hoseini, *Bull. Korean Chem. Soc.*, 33, 2140 (2012).
- [4] M. Bakavoli, V.R. Hedayati, M.M. Heravi, A. Davoodnia, H. Eshghi, *Chem. Sci. Trans.*, 1, 341 (2012).
- [5] H. Mirzaei, A. Davoodnia, *Chin. J. Catal.*, 33, 1502 (2012).
- [6] K. Sayama, H. Arakawa, *J. Phys. Chem.*, 97, 531 (1993).
- [7] F. Taghavi-Khorasani, A. Davoodnia, *Res. Chem. Intermediat.*, 41, 2415 (2015).
- [8] T. Hideo, and J. Teruomi, *Jpn. Pat*, 56005480, 20 (1981).
- [9] J.P. Poupelin, G. Saint-Ruf, O. Foussard-Blanpin, G. Marcisse, G. Uchida-Ernouf, R. Lacroix, *Eur. J. Med. Chem.*, 13, 67 (1978).
- [10] R.W. Lamberk, J.A. Martin, J.H. Merrett, K.E.B. Parkes, G.J. Thomas, PCT Int. Appl. WO 9706178, 1997. In *Chem. Abstr.*, 126, 212377y (1977).
- [11] G. Saint-Ruf, J.P. Poupelin, *Naturwissenschaften*, 62, 584 (1975).
- [12] R.M. Ion, D. Frackowiak, A. Planner, K. Wiktorowicz, *Acta Biochim. Pol.*, 45, 833 (1998).
- [13] A. Banerjee, A.K. Mukherjee, *Stain Technol.*, 56, 83 (1981).

- [14] C.G. Knight, T. Stephens, *Biochem. J.*, 258, 683 (1989).
- [15] M. Ahmad, T.A. King, D.K. Ko, B.H. Cha, J. Lee, *J. Phys. D: Appl. Phys.*, 35, 1473 (2002).
- [16] N.V. Shitole, S.B. Sapkal, B.B. Shingate, M.S. Shingare, *Bull. Korean Chem. Soc.*, 32, 35 (2011).
- [17] V. Rama, K. Kanagaraj, K. Pitchumani, *Tetrahedron Lett.*, 53, 1018 (2012).
- [18] X.J. Sun, J.F. Zhou, P.S. Zhao, *Synth. Commun.*, 42, 1542 (2012).
- [19] M. Zakeri, M.M. Heravi, M. Saeedi, N. Karimi, H.A. Oskooie, N. Tavakoli-Hoseini, *Chin. J. Chem.*, 29, 1441 (2011).
- [20] M. Sadeghpour, A. Olyaei, M. Rezaei, *J. Heterocycl. Chem.*, 53, 981 (2016).
- [21] F. Shirini, S. Akbari-Dadamahaleh, A. Mohammad-Khah, A.R. Aliakbar, *C. R. Chimie*, 16, 207 (2013).
- [22] J.M. Khurana, D. Magoo, *Tetrahedron Lett.*, 50, 4777 (2009).
- [23] Z.H. Zhang, P. Zhang, S.H. Yang, H.J. Wang, J. Deng, *J. Chem. Sci.*, 122, 427 (2010).
- [24] L.P. Mo, H.L. Chen, *J. Chin. Chem. Soc.*, 57, 157 (2010).
- [25] S. Sudha, M.A. Pasha, *Ultrason. Sonochem.*, 19, 994 (2012).
- [26] F. Taghavi-Khorasani, A. Davoodnia, *Res. Chem. Intermed.*, 41, 2415 (2015).
- [27] B. Das, K. Laxminarayana, M. Krishnaiah, Y. Srinivas, *Synlett*, 2007, 3107 (2007).
- [28] G.C. Nandi, S. Samai, R. Kumar, M.S. Singh, *Tetrahedron*, 65, 7129 (2009).
- [29] H.J. Wang, X.Q. Ren, Y.Y. Zhang, Z.H. Zhang, *J. Braz. Chem. Soc.*, 20, 1939 (2009).
- [30] M.M. Heravi, H. Alinejhad, K. Bakhtiari, H.A. Oskooie, *Mol. Divers.*, 14, 621 (2010).
- [31] J. Li, W. Tang, L. Lu, W. Su, *Tetrahedron Lett.*, 49, 7117 (2008).
- [32] A. Nakhaei, A. Davoodnia, *Chin. J. Catal.*, 35, 1761 (2014).
- [33] A. Nakhaei, A. Davoodnia, A. Morsali, *Res. Chem. Intermed.*, 41, 7815 (2015).
- [34] A. Davoodnia, A. Nakhaei, N. Tavakoli-Hoseini, *Z. Naturforsch. B*, 71, 219 (2016).
- [35] M. Rohaniyan, A. Davoodnia, A. Nakhaei, *Appl. Organometal. Chem.*, 30, 626 (2016).
- [36] E. Kolvari, N. Koukabi, M.M. Hosseini, M. Vahidian, E. Ghobadi, *RSC Advances*, 6, 7419 (2016).
- [37] A. Amoozadeh, S. Rahmani, M. Bitaraf, F.B. Abadi, E. Tabrizian, *New J. Chem.*, 40, 770 (2016).