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Synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one Catalyzed by Silica Sulfuric Acid Under Solvent Free Condition

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Abstract: An efficient synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one derivatives *via* the threecomponent condensation of aromatic aldehyde, 2-naphthol and 5,5-dimethyl-1,3-cyclohexanedione was carried out in 72-85% yields at 80 °C under solvent free condition using silica sulfuric acid (SSA) as catalyst.

Keywords: Silica sulfuric acid, three-component condensation, xanthene.

INTRODUCTION

Xanthenes and benzoxanthenes are important biologically active heterocyclic compounds, which possess antiviral [1], antibacterial [2] and anti-inflammatory activities [3]. These compounds can be used as dyes [4, 5], pH-sensitive fluorescent materials [6] and in laser technology [7]. Synthesis of these compounds via threecomponent condensation of aldehyde, 2-naphthol and cyclic 1,3-dicarbonyl compounds was carried out under different conditions, such as solvent-free reaction catalyzed by HBF₄/SiO₂ [8], I₂ [9], *p*-TSA [10, 11], InCl₃ or P₂O₅ [12], Zr(HSO₄)₄ [13], H₃PW₁₂O₄₀ [14], cyanuric chloride [15], HClO₄-SiO₂ [16], CAN [17], and refluxing in 1,2dichloroethane catalyzed by Sr(OTf)₂ [18] or NaHSO₄·SiO₂ [19]. However, in spite of their potential utility, some of the reported methods suffer from some draw-backs, such as longer reaction time, use of expensive transition metal catalyst or hazardous solvent. Hence, the development of new and simple synthetic methods for the preparation of heterocyclic compounds containing xanthone fragment remains an interesting challenge.

Catalysts supported on inorganic substrates have received increasing attention in recent years as a means to develop more convenient or selective catalysts [20]. SSA is a good proton source and an excellent candidate for sulfuric acid or chlorosulfonic acid replacement in organic reactions without any limitation such as destruction of acid sensitive functional groups, use of rather toxic solvents and expensive reagents or solvents [21]. Because of its advantages such as stable, easy production, insolubility in all organic solvent, reusable, cheap and facile, SSA has been used as catalyst in some organic reactions [22].

In continuation of our investigation on application of SSA in organic synthesis [23, 24], we wish to report the onepot synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a] xanthen-11-one catalyzed by SSA under solvent free condition (Scheme 1).

RESULTS AND DISCUSSION

To optimize the reaction conditions, the condensation of benzaldehyde, 2-naphthol and 5,5-dimethyl-1,3-cyclohexanedione was selected as the model under solvent free condition catalyzed by SSA. A series of experiments at varying temperature were carried out. As shown in Table 1, when the reaction was carried out at 70 °C, it took 30 min to obtain compound 4 in 80% yield (Entry 1), while when the temperature was 80 °C and 100 °C, the reaction time was shortened to 20 min and the yield was 81% (Entry 2) and 83% (Entry 3) respectively. It indicates that reaction temperature had a little effect on the reaction.

The effect of amount of SSA on the reaction was studied. When the amount of SSA was 5 mol% and 10 mol%, the yield of **4i** was 75% (Entry **4**) and 81% (Entry **2**) respectively. While increasing the amount of silica sulfuric acid to 15 mol% (Entry **5**), no improvement was observed on both the yield and the reaction time compared with that at 10 mol% (Entry **2**).

The effect of molar ratio of reactants on reaction was investigated. As shown in Table 1, when molar ratio of benzaldehyde, 2-naphthol and 5,5-dimethyl-1,3-cyclohexanedione was 1:1:1, 1:1:1.2 and 1.2:1:1.2 respectively, the best yield of 9,9-dimethyl-12-phenyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one was achieved

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Scheme 1. Synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one

 Table 1.
 The Effect of Reaction Conditions on the Synthesis of 9,9-dimethyl-12-phenyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11one

Entry	Amount of SSA/mol%	Molar ratio of 1: 2: 3	Temperature/°C	Reaction time/min.	Isolated yield/%
1	10	1:1:1	70	30	80
2	10	1:1:1	80	20	81
3	10	1:1:1	100	20	83
4	5	1:1:1	80	20	75
5	15	1:1:1	80	20	81
6	10	1:1:1.2	80	20	81
7	10	1.2:1:1.2	80	40	86

(86%, Table 1, Entry 7) but with molar ratio of 1.2:1:1.2, the reaction time increased to 40 min. Considering the amount of benzaldehyde and 5,5-dimethyl-1,3-cyclohexanedione both were increased by 20% while the yield was only increased by 5%, so the molar ratio of benzaldehyde, 2-naphthol and 5,5-dimethyl-1,3-cyclohexanedione was chosen to 1:1:1.

From the results given in Table 1, the reaction conditions we chose were as follows: aromatic aldehyde (1, 1 mmol), 2-naphthol (2, 1 mmol), 5,5-dimethyl-1,3-cyclohexanedione (3, 1 mmol), SSA (0.1 mmol), reaction temperature 80 °C. Using this reaction system, a series of experiments for the synthesis of **4a-i** were carried out. The results were summarized in Table 2. As shown in Table 2, all reactions can be finished in 30 min except 4-hydroxybenzaldehyde (65 min) to give the products in 72-85% yields. In the present procedure, aromatic aldehydes with electron-donating substituents or electron-withdrawing substituents have a little effect on the yield.

From these results listed in Table 2, we can deduce that the yields are in general, similar or a little lower than those described in literatures [8-19, 25-26], but the reaction time was greatly decreased. For example, in the previous report [18], the condensation of 4-chlorobenzaldehyde, 2-naphthol 5,5-dimethyl-1,3-cyclohexanedione and catalyzed by Sr(OTf)₂ at refluxing temperature in ClCH₂CH₂Cl for 5 h, the yield of 4e was 85%; in the reaction catalyzed by NaHSO₄·SiO₂ [19], the condensation of benzaldehyde, 2naphthol and 5,5-dimethyl-1,3-cyclohexanedione was carried out in 87% yield under refluxing 1,2-dichloroethane for 4 h, while present procedure needed only 20 min to afford target product in 81% yield (Table 2, 4i).

The recycling performance of catalyst in the same model condensation reaction was also investigated. After completion of the reaction, the reaction mixture was dissolved in dicholoromethane to precipitate the catalyst. The organic layer was separated and the catalyst was used

Entry	R	Reaction time/min	Product	Isolated yield/%	m. p. /°C (Ref.)
а	3-NO ₂	20	4a	78	168-169 (168–170) [25]
b	4-NO ₂	20	4b	81	179-180 (178-180) [24]
с	2-Cl	20	4c	82	178-179 (179-180) [24]
d	3-C1	30	4d	85	180-181 (180-181) [26]
e	4-C1	20	4e	80	183-184 (182-183) [27]
f	4-CH ₃	30	4f	72	180-181 (176-177) [28]
g	4-OCH ₃	30	4g	73	209-210 (208-209) [29]
h	4-OH	65	4h	74	212-213 (213-214) [27]
i ^a	Н	20	4i	81, 75, 72, 72	152-153 (152-153) [27]

Table 2. Synthesis of 4a-i catalyzed by SSA at 80 °C Under Solvent Free

^aCatalyst was reused three times.



Scheme 2. Preparation of silica sulfuric acid.

directly for next run after removing the residual solvent. The catalyst at least can be reused three times without significant decrease in activity. Yields remained practically constant (72-75%, Table 2, 4i) over three catalyst cycling experiments.

In conclusion, the SSA can catalyze three-component one-pot synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo [a]xanthen-11-one *via* the condensation of aromatic aldehyde, 2-naphthol and 5,5-dimethyl-1,3-cyclohexanedione under solvent free condition to offer a moderate yield.

EXPERIMENTAL

Melting points were determined with a SGW X-4 microscopic melting point apparatus (Shanghai Precision & Scientific Instrument Co., Ltd, P. R. China) in open capillaries and are uncorrected. The ¹H NMR spectra were recorded on Bruker AVANCE III 600 (600 MHz) spectrometer using TMS as internal standard and CDCl₃ as solvent.

SSA was prepared according to the method reported in literature [30].

A 500 mL suction flask was used. It was equipped with a constant-pressure dropping funnel containing chlorosulfonic acid (23.3 g, 0.2 mol) and gas inlet tube for conducting HCl gas over an adsorbing solution i.e. water. Into it were charged 60.0 g of silica gel. Cholorosulfonic acid was added dropwise over a period of 30 min at room temperature. HCl gas evolved from the reaction vessel immediately (Scheme 2). After the addition was complete the mixture was shaken for 30 min. A white solid (silica sulfuric acid) of 76.0 g was obtained.

General Procedure for the Synthesis of title Compound 4a-i

A 5 mL flask was charged with aromatic aldehydes (1, 1 mmol), 2-naphthol (2, 1 mmol), 5,5-dimethyl-1,3cyclohexanedione (3, 1 mmol) and silica sulfuric acid (0.1 mmol). The reaction mixture was stirred at 80 °C for the period of time as indicated in Table 2. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was diluted with dicholoromethane to precipitate the catalyst, which was used directly for next run after removing the residual solvent. The organic layer was separated and dried over anhydrous sodium sulfate, filtered and evaporated to dryness in vacuo to give the crude product, which was separated by column chromatography on silica gel (200-300 mesh), eluted with petroleum ether (bp 60-90 °C) or a mixture of petroleum ether and ethyl acetate to offer product 4a-i. These products were known compounds, which was established by ¹H NMR and their melting point compared with that reported in the literatures.

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

White solid, ¹HNMR: $\delta_{\rm H}$ 0.95 (s, 3H, CH₃), 1.13 (s, 3H, CH₃), 2.24 (d, J = 16.3 Hz, 1H, CH₂), 2.33 (d, J = 16.3 Hz, 1H, CH₂), 2.61 (s, 2H, CH₂), 5.82 (s, 1H, CH), 7.35-7.46 (m, 4H, Ph-H), 7.79-7.82 (m, 3H, Ph-H), 7.86 (d, J = 8.2 Hz, 1H, Ph-H), 7.92-7.94 (m, 1H, Ph-H), 8.11 (s, 1H, Ph-H).

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

White solid, ¹H NMR: $\delta_{\rm H}$ 0.94 (s, 3H, CH₃), 1.13 (s, 3H, CH₃), 2.24 (d, J = 16.3 Hz, 1H, CH₂), 2.32 (d, J = 16.3 Hz, 1H, CH₂), 2.57 (d, J = 17.6 Hz, 1H, CH₂), 2.61 (d, J = 17.6 Hz, 1H, CH₂), 5.81 (s, 1H, CH), 7.35 (d, J = 8.9 Hz, 1H, Ph-H), 7.38-7.41 (m, 1H, Ph-H), 7.42-7.45 (m, 1H, Ph-H), 7.50 (m, 2H, Ph-H), 7.79-7.83 (m, 3H, Ph-H), 8.02-8.04 (m, 2H, Ph-H).

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

White solid, ¹H NMR: $\delta_{\rm H}$ 1.00 (s, 3H, CH₃), 1.14 (s, 3H, CH₃), 2.26 (d, J = 16.3 Hz, 1H, CH₂), 2.31 (d, J = 16.3 Hz, 1H, CH₂), 2.59 (d, J = 17.4 Hz, 1H, CH₂), 2.62 (d, J = 17.4 Hz, 1H, CH₂), 5.99 (s, 1H, CH), 6.97-7.00 (m, 1H, Ph-H), 7.05 (t, J = 7.1 Hz, 1H, Ph-H), 7.26-7.30 (m, 3H, Ph-H), 7.38 (t, J = 7.2 Hz, 1H, Ph-H), 7.48 (t, J = 7.1 Hz, 1H, Ph-H), 7.75 (t, J = 9.1 Hz, 2H, Ph-H), 8.22 (d, J = 8.5 Hz, 1H, Ph-H).

12-(3-Chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4d)

White solid, ¹H NMR: $\delta_{\rm H}$ 0.98 (s, 3H, CH₃), 1.12 (s, 3H, CH₃), 2.26 (d, J = 16.3 Hz, 1H, CH₂), 2.31 (d, J = 16.3 Hz, 1H, CH₂), 2.56 (d, J = 17.4 Hz, 1H, CH₂), 2.59 (d, J = 17.6 Hz, 1H, CH₂), 5.69 (s, 1H, CH), 7.02-7.04 (m, 1H, Ph-H), 7.11 (t, J = 7.9 Hz, 1H, Ph-H), 7.25-7.29 (m, 2H, Ph-H), 7.33 (d, J = 8.9Hz, 1H, Ph-H), 7.38-7.40 (m, 1H, Ph-H), 7.46 (m, 1H, Ph-H), 7.79 (t, J = 7.7 Hz, 2H, Ph-H), 7.92 (d, J = 8.5 Hz, 1H, Ph-H).

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

White solid, ¹H NMR: $\delta_{\rm H}$ 0.96 (s, 3H, CH₃), 1.11 (s, 3H, CH₃), 2.24 (d, J = 16.3 Hz, 1H, CH₂), 2.30 (d, J = 16.3 Hz, 1H, CH₂), 2.56 (s, 2H, CH₂), 5.68 (s, 1H, CH), 7.12-7.14 (m, 2H, Ph-H), 7.26-7.28 (m, 2H, Ph-H), 7.31 (d, J = 8.9 Hz, 1H, Ph-H), 7.37-7.39 (m, 1H, Ph-H), 7.42-7.44 (m, 1H, Ph-H), 7.77 (t, J = 8.6 Hz, 2H, Ph-H), 7.90 (d, J = 8.5 Hz, 1H, Ph-H).

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

White solid, ¹H NMR: $\delta_{\rm H}$ 0.97 (s, 3H, CH₃), 1.11 (s, 3H, CH₃), 2.19 (s, 3H, CH₃), 2.24 (d, J = 16.2 Hz, 1H, CH₂), 2.30 (d, J = 16.2 Hz, 1H, CH₂), 2.56 (s, 2H, CH₂), 5.66 (s, 1H, CH), 6.96 (d, J = 7.9 Hz, 2H, Ph-H), 7.21-7.22 (m, 2H, Ph-

H), 7.31 (d, *J* = 8.9 Hz, 1H, Ph-H), 7.34-7.37 (m, 1H, Ph-H), 7.41-7.44 (m, 1H, Ph-H), 7.74 (d, *J* = 8.9 Hz, 1H, Ph-H), 7.76 (d, *J* = 7.9 Hz, 1H, Ph-H), 8.0 (d, *J* = 8.5 Hz, 1H, Ph-H).

12-(4-Methoxyphenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one (4g)

White solid, ¹H NMR: $\delta_{\rm H}$ 0.97 (s, 3H, CH₃), 1.11 (s, 3H, CH₃), 2.24 (d, J = 16.3 Hz, 1H, CH₂), 2.30 (d, J = 16.3 Hz, 1H, CH₂), 2.55 (s, 2H, CH₂), 3.68 (s, 3H, CH₃), 5.65 (s, 1H, CH), 6.69-6.71 (m, 2H, Ph-H), 7.23-7.25 (m, 2H, Ph-H), 7.30 (d, J = 8.9 Hz, 1H, Ph-H), 7.35-7.37 (m, 1H, Ph-H), 7.41-7.44 (m, 1H, Ph-H), 7.74 (d, J = 8.9 Hz, 1H, Ph-H), 7.76 (d, J = 7.9 Hz, 1H, Ph-H), 7.98 (d, J = 8.5 Hz, 1H, Ph-H).

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

White solid, ¹H NMR: $\delta_{\rm H}$ 0.96 (s, 3H, CH₃), 1.10 (s, 3H, CH₃), 2.26 (d, J = 16.3 Hz, 1H, CH₂), 2.31 (d, J = 16.3 Hz, 1H, CH₂), 2.56 (s, 2H, CH₂), 5.63 (s, 1H, CH), 6.14 (s, 1H, OH), 6.59 (d, J = 8.6 Hz, 2H, Ph-H), 7.15-7.43 (m, 5H, Ph-H), 7.74 (d, J = 8.9 Hz, 1H, Ph-H), 7.77 (d, J = 7.9 Hz, 1H, Ph-H), 7.97 (d, J = 8.4 Hz, 1H, Ph-H).

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

White solid, ¹H NMR: $\delta_{\rm H}$ 0.95 (s, 3H, CH₃), 1.11 (s, 3H, CH₃), 2.24 (d, J = 16.3 Hz, 1H, CH₂), 2.30 (d, J = 16.3 Hz, 1H, CH₂), 2.56 (s, 2H, CH₂), 5.70 (s, 1H, CH), 7.03-7.06 (m, 1H, Ph-H), 7.15-7.17 (m, 2H, Ph-H), 7.31-7.34 (m, 4H, Ph-H), 7.40-7.43 (m, 1H, Ph-H), 7.76 (t, J = 9.2 Hz, 2H, Ph-H), 7.98 (d, J = 8.4 Hz, 1 H, Ph-H).

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CONFLICT OF INTEREST

Declared none.

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