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Phosphoric acid supported on alumina (H_3PO_4/Al_2O_3) as an efficient and reusable catalyst for the one-pot synthesis of benzoxanthene pigments

Hamid Reza Shaterian · Kobra Azizi · Nafiseh Fahimi

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Abstract Phosphoric acid supported on alumina (H_3PO_4/Al_2O_3) is an efficient catalyst for the catalytic multi-component condensation reaction and a wide variety of syntheses of benzoxanthene pigments in good yields. The remarkable features of this new procedure are high conversions, shorter reaction times, cleaner reaction, and simple experimental and work-up procedures.

Keywords Phosphoric acid · Alumina · Benzoxanthene · Heterogeneous catalyst · Solvent-free

Introduction

Multi-component processes have recently gained considerable economic and ecological interest, as they direct to specific destinations essential principles of synthetic efficiency and reaction design. Multi-component reactions (MCRs) have been proven to be a very refined and rapid way to access complex structures in a single synthetic operation from simple building blocks and show high atom economy and high selectivity [1].

Dyes have played an essential role in human history since primeval days. Dyes are used in almost every commercial product such as food, clothing, pigments and paints, etc. [2].

Derivatives of xanthene are commonly referred to collectively as xanthenes, and among other uses are the basis of a class of dyes which includes fluorescein, eosins, and rhodamines. Xanthene dyes tend to be fluorescent, yellow to pink to bluish red, brilliant dyes [3].

H. R. Shaterian (✉) · K. Azizi · N. Fahimi
Department of Chemistry, Faculty of Sciences, University of Sistan and Baluchestan,
PO Box 98135-674, Zahedan, Iran
e-mail: hrshaterian@chem.usb.ac.ir

Xanthenes are crystalline organic compounds in which two benzene rings are fused to a central pyran ring [4]. It is a parent chemical structure of many medicinal elements and is a useful intermediate in organic synthesis [5]. Xanthenes nuclei are used chiefly in dyeing textile fibers, coloring paper, producing fluorescent effects, and as organic pigments [6].

Thus, the synthesis of a variety of xanthene heterocyclic molecules is important for researchers. Phosphoric acid-supported alumina was prepared for the first time by Araujoa et al. [7] by the mixing of alumina with phosphoric acid. This heterogeneous catalyst was characterized and the catalytic evaluation of oleic acid conversion to biofuels and biolubricants was studied. The best catalytic performance was achieved with the highest surface area alumina impregnated with H_3PO_4, which was the solid that allied high total acidity with a large quantity of mesopore surface area. According to the ^{31}P NMR data, two structures for the catalyst were confirmed [8]: (1) different phosphorous and aluminum interactions in bridging structures, and (2) linear phosphorous and aluminum bonding (Scheme 1).

In the mainstream of the current interest of research on solid heterogeneous acidic catalysts, we wish to describe a new protocol for the rapid synthesis of benzoxanthenes from the three-component condensation reaction under thermal solvent-free conditions with a catalytic amount of H_3PO_4/Al_2O_3 (50 % w/w) as a catalyst (Scheme 2).

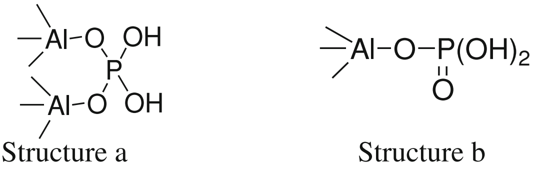
Experimental

Materials and methods

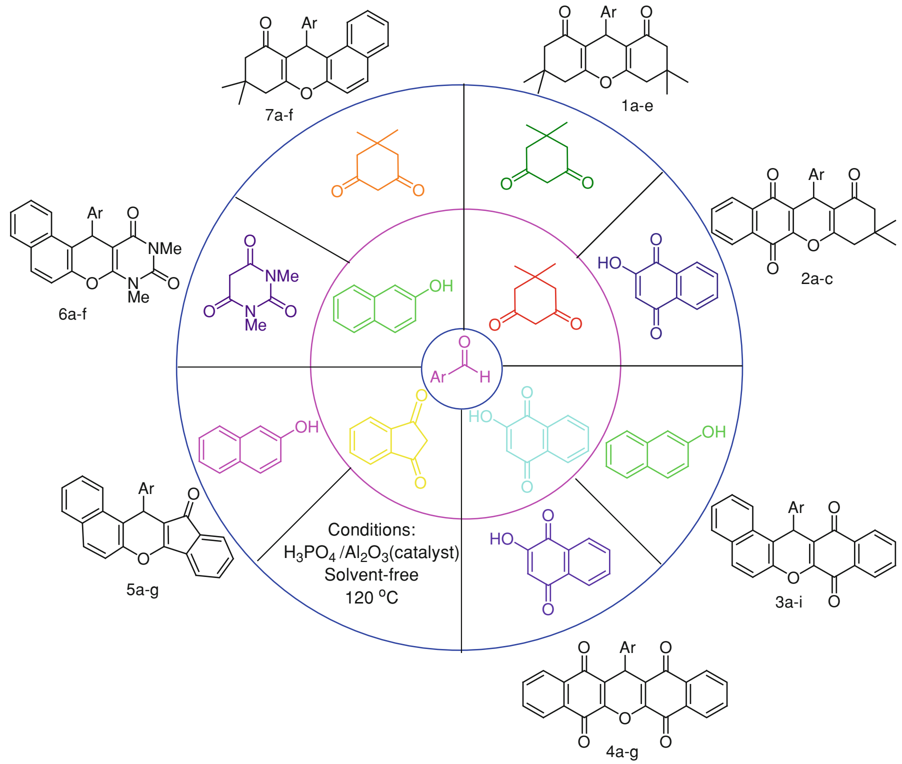
All reagents were purchased from Merck and Sigma–Aldrich and used without further purification. H_3PO_4/Al_2O_3 (50 % w/w) was prepared according to the reported procedure [7]. All yields refer to isolated products after purification. The NMR spectra were recorded on a Bruker Avance DPX 500, 400 MHz instrument. IR spectra were recorded on a JASCO FT-IR 460 plus spectrophotometer. Melting points were determined in open capillaries with a BUCHI 510 melting point apparatus. TLC was performed on silica–gel polygram SILG/UV 254 plates.

Synthesis of 3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-aryl-2*H*-xanthene-1,8(5*H*,9*H*)-dione(**1a–e**)

Aldehyde (1.0 mmol) and dimedone (2 mmol) were ground and 100 mg of (H_3PO_4/Al_2O_3) (50 % w/w) was added to the reaction mixture, which was heated in an oil bath at 120 °C for the appropriate times (**1a–e**) which was monitored by TLC. After



Scheme 1 Two structures for phosphoric acid-supported alumina



Scheme 2 Synthesis of benzoxanthenes

satisfactory completion, the reaction mass was cooled to 25 °C, then the solid residue was dissolved in dichloromethane. The catalyst was washed twice with (2 × 5 ml) dichloromethane. The recovered catalyst was dried in 100 °C. The filtrate solution was evaporated and the solid product was purified by a recrystallization procedure in aqueous EtOH (25 %).

Synthesis of 3,4-dihydro-3,3-dimethyl-12-aryl-2*H*-benzo[*b*]xanthene-1,6,11 (12*H*)-trione (**2a–i**) and 14-aryl-14*H*-dibenzo[*a,i*]xanthene-8,13-diones(**3a–i**)

A stirred mixture of arylaldehydes (1 mmol), dimedone (**2a–i**) or *β*-naphthol (**3a–i**) (1 mmol), 2-hydroxy-1,4-naphthoquinone (1 mmol), and (H_3PO_4/Al_2O_3) (50 % w/w, 100 mg) was reacted in an oil bath at 120 °C for the appropriate times. Completion of the reaction was indicated by TLC, after which it was cooled to room temperature and the crude solid product was dissolved in dichloromethane, and filtered for separation of the catalyst. The catalyst was washed twice with dichloromethane (2 × 5 ml), and then the recovered catalyst was dried in an oven at 100 °C for 3 h. The filtered organic solution was concentrated. The solid product was purified by recrystallization procedure in aqueous EtOH (15 %).

Select characterizations of the orange–red products are given below.

*3,4-Dihydro-3,3-dimethyl-12-phenyl-2H-benzo[b]xanthene-1,6,11(12H)-trione(**2a**)*

Orange powder; mp: 264–265 °C; ^{1}H NMR (500 MHz, DMSO-d_6): $\delta = 0.94$ (3H, s), 1.07 (3H, s), 2.15 and 2.31 (2H, s), 2.67 (2H, s), 4.88 (1H, s), 7.10–7.15 (1H, m), 7.21–7.32 (2H, m), 7.43–7.46 (2H), 7.80–7.91 (3H, m), 7.99–8.07 (1H, m). ^{13}C NMR (125 MHz, DMSO-d_6): $\delta = 26.9$, 28.9, 32.4, 32.7, 40.1, 113.6, 124.2, 126.2, 126.5, 127.2, 128.7, 128.8, 129.0, 130.9, 131.4, 134.6, 135.0, 143.2, 149.5, 163.4, 177.5, 183.2, 196.3 ppm; IR (KBr) (υ_{max}, cm^{-1}): 2,926, 1,678, 1,606.

*14-(3,4,5-Trimethoxylphenyl)-14H-dibenzo[a,i]xanthene-8,13-dione(**3h**)*

Orange powder; mp: 288–290 °C; ^{1}H NMR (500 MHz, DMSO-d_6): $\delta = 3.71$ (s, 3H), 3.73 (s, 6H), 6.57 (s, 2H), 7.41–7.56 (m, 4H), 7.74–7.77 (m, 1H), 7.82–7.89 (m, 2H), 7.95 (d, $J = 8.01$, 1H), 8.06–8.13 (m, 2H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): $\delta = 178.4$, 178.38, 157.16, 153.18, 147.35, 138.70, 136.82, 135.21, 131.9, 131.3, 131.12, 130.85, 129.96, 129.7, 129.45, 128.60, 127.56, 125.69, 124.59, 123.84, 116.73, 116.56, 116.34, 105.88, 77.51, 77.09, 77.66, 60.72, 56.11,35.28 ppm; IR (KBr) (υ_{max}, cm^{-1}): 3,035, 1,700, 1,655, 1,636, 1,617, 1,589, 1,543, 1,507, 1,458, 1,286, 1,213, 1,126, 1,092.

*14-(2,5-Dimethoxylphenyl)-14H-dibenzo[a,i]xanthene-8,13-dione(**3i**)*

Orange powder; mp: 260 °C; ^{1}H NMR (500 MHz, DMSO-d_6): $\delta = 3.63$ (s, 3H), 3.92 (s, 3H), 6.11 (s, 1H), 6.61–6.58 (m, 1H), 6.77 (d, $J = 8.91$ 1H), 6.84 (d, $J = 2.82$, 1H), 7.37–7.50 (m, 3H), 7.55 (t, $J = 7.56$, 1H), 7.74–7.80 (m,3H), 8.09 (d, $J = 7.59$, 1H), 8.15 (d, $J = 7.77$, 1H), 8.26 (d, $J = 8.37$, 1H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): $\delta = 178.5$, 178.18, 157.4, 153.7, 151.1, 147.0, 135.1, 133.4, 131.7, 131.9, 131.1, 130.1, 129.3, 129.1, 128.4, 127.3, 125.4, 124.5, 124.1, 117.5, 117.2, 116.8, 116.2, 113.1, 112.1, 57.0, 55.5, 30.0 ppm; IR (KBr) (υ_{max}, cm^{-1}): 3,034, 1,698, 1,655, 1,637, 1,590, 1,542, 1,508, 1,499, 1,458, 1,289, 1,214, 1,182, 1,155.

Synthesis of 13-aryl-5*H*- dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraones(**4a–i**):

A stirred mixture of aldehyde (1 mmol), 2-hydroxy-1,4-naphthoquinone (2 mmol) and (H_3PO_4/Al_2O_3) (50 % w/w, 100 mg) was reacted in an oil bath at 120 °C for the appropriate times (Table 1). Completion of the reaction was indicated by TLC, after which it was cooled to room temperature and the crude solid product was dissolved in dichloromethane, and filtered for separation of the catalyst. The catalyst was washed twice times with dichloromethane (2 × 5 ml), and then the recovered catalyst was dried in an oven at 100 °C for 3 h. The filtered organic solution was concentrated. The solid product was purified by recrystallization procedure in aqueous EtOH (15 %).

Select characterizations of the orange–red products are given below.

*13-Phenyl-5H-dibenzo[b,i]xanthene-5,7,12,14(13H)-tetraone(**4a**)*

Red powder; mp: 305–307 °C; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 5.09$ (1H, s), 7.16–8.08 (13H, m) ppm. IR (KBr, cm^{-1}): 3,035, 1,660, 1,569.

*13-(4-chlorophenyl)-5H-dibenzo[b,i]xanthene-5,7,12,14(13H)-tetraone(**4b**)*

Orange powder; mp: 330–332 °C. ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 5.10$ (1H, s), 7.26–8.07 (12H, m) ppm. IR (KBr, cm^{-1}): 3,028, 1,663, 1,610.

*13-(p-Tolyl)-5H-dibenzo[b,i]xanthene-5,7,12,14(13H)-tetraone(**4e**)*

Brick-red powder; mp: 304–307 °C; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 2.21$ (3H, s), 5.09 (1H, s), 7.07–8.12 (12H, m) ppm. IR (KBr, cm^{-1}): 3,088, 1,663, 1,608.

*13-(3-Nitrophenyl)-5H-dibenzo[b,i]xanthene-5,7,12,14(13H)-tetraone(**4g**)*

Orange powder; mp: 340–342 °C; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 5.47$ (1H, s), 7.11–8.13 (12H, m) ppm. IR (KBr, cm^{-1}): 3,035, 1,662, 1,605.

Synthesis of 13-aryl-indeno[1,2-*b*]naphtha[1,2-*e*]pyran-12(13*H*)-ones(**5a–g**):

A stirred mixture of *β*-naphthol (1 mmol), aldehyde (1 mmol), 2*H*-indene-1,3-dione (1 mmol) and 100 mg of (H_3PO_4/Al_2O_3) was reacted in an oil bath at 120 °C for the appropriate times. When the reaction was completed, it was cooled to room temperature and the crude solid product was dissolved in dichloromethane, and filtered for separation of the catalyst. The catalyst was washed twice times with dichloromethane (2 × 5 ml), and then the recovered catalyst was dried in an oven at 100 °C for 3 h. The filtered organic solution was concentrated. The solid product was purified by recrystallization procedure in aqueous EtOH (15 %).

Select characterizations of the orange–red products are given below.

*13-(4-Chlorophenyl)-indeno[1,2-b]naphtho[1,2-e]pyran-12(13H)-one(**5b**)*

Yellow solid; mp: 225–226 °C; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.88$–7.84 (m, 2H), 7.75 (t, $J = 9.2$ Hz, 1H), 7.51 (d, $J = 8.8$ Hz, 1H), 7.45–7.25 (m, 8H), 7.18 (d, $J = 8.4$ Hz, 2H), 5.63 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDC13) $\delta = 192.3$, 167.3, 149.0, 142.1, 136.7, 132.3, 132.2, 131.9, 131.6, 130.2, 129.9, 129.5, 128.7, 128.6, 127.3, 125.4, 124.2, 121.7, 118.4, 117.7, 116.0, 110.4, 35.1 ppm.

*13-(4-Methylphenyl)-indeno[1,2-b]naphtho[1,2-e]pyran-12(13H)-one(**5d**)*

Yellow solid; mp: 192–193 °C; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.88$–7.82 (m, 3H), 7.50 (d, $J = 9.2$ Hz, 1H), 7.43–7.28 (m, 6H), 7.21 (d, $J = 8.0$ Hz, 2H), 7.02 (d, $J = 8.0$ Hz, 2H), 5.61 (s, 1H), 2.24 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 192.4$, 167.2, 149.0, 140.8, 136.9, 136.1, 132.4, 132.2, 131.9, 130.0, 129.5,

Table 1 Synthesis of benzoxanthene pigments using H_3PO_4/Al_2O_3 (50 % w/w) as a catalyst at 120 °C under solvent-free conditions

Entry	Aldehyde	Time (min)	Yield (%)[a]	Melting points (°C)	
				Found	Lit [Ref]
1a	Benzaldehyde	25	90	206–208	205–206 [15]
1b	4-Methoxybenzaldehyde	30	84	240–242	241–243 [15]
1c	2-Cholorobenzaldehyde	25	82	226–227	226–228 [15]
1d	4-Nitrobenzaldehyde	20	90	221–223	221–223 [15]
1e	3-Nitrobenzaldehyde	20	92	168–170	167–168 [15]
2a	Benzaldehyde	30	87	264–265	263–265 [16]
2b	4-Cholorobenzaldehyde	25	90	283	282–284 [16]
2c	4-Bromobenzaldehyde	35	84	268–270	268–270 [16]
3a	Benzaldehyde	20	95	319–320	319–320 [17]
3b	4-Nitrobenzaldehyde	15	90	333–335	332–333 [17]
3c	3-Nitrobenzaldehyde	15	95	305–306	304–305 [17]
3d	2,4-Dicholorobenzaldehyde	8	89	302–303	301–302 [17]
3e	4-Cholorobenzaldehyde	5	93	305–307	305–306 [17]
3f	4-Methylbenzaldehyde	18	87	256–258	255–256 [17]
3g	4-Methoxybenzaldehyde	15	90	279–281	279–280 [17]
3h	3,4,5-Trimethoxybenzaldehyde	25	86	288–290	288–290 [18]
3i	2,5-Dimethoxybenzaldehyde	15	89	260	260 [18]
4a	Benzaldehyde	10	91	305–307	305–307 [19]
4b	4-Cholorobenzaldehyde	10	93	332–334	330–332 [19]
4c	4-Bromobenzaldehyde	10	95	334–336	333–335 [19]
4d	4-Flourobenzaldehyde	8	84	270–272	270–272 [19]
4e	4-Methylbenzaldehyde	15	90	304–306	304–307 [19]
4f	2-Cholorobenzaldehyde	12	92	308–310	307–309 [19]
4g	3-Nitrobenzaldehyde	8	93	340–342	340–342 [19]
5a	Benzaldehyde	40	82	200–202	202–203 [20]
5b	4-Cholorobenzaldehyde	28	85	225–226	225–226 [20]
5c	3-Nitrobenzaldehyde	45	78	243–245	240–241 [20]
5d	4-Methylbenzaldehyde	40	75	192–193	192–193 [20]
5e	2,4-Dicholorobenzaldehyde	45	80	251	252–253 [20]
5f	2-Cholorobenzaldehyde	40	73	242–243	240–241 [20]
5g	4-Methoxybenzaldehyde	35	88	225–226	225–226 [20]
6a	Benzaldehyde	55	85	226–228	226–228 [21]
6b	4-Methylbenzaldehyde	50	82	198	196–198 [21]
6c	2,4-Dicholorobenzaldehyde	60	80	223–225	222–224 [21]
6d	4-Nitrobenzaldehyde	50	87	288–290	288–290 [21]
6e	4-Cholorobenzaldehyde	55	78	270–272	270–272 [21]
6f	4-Bromobenzaldehyde	55	75	244–245	243–245 [21]
7a	Benzaldehyde	20	90	151–153	149–150 [22]
7b	4-Nitrobenzaldehyde	25	91	178–180	178–181 [22]

Table 1 continued

Entry	Aldehyde	Time (min)	Yield (%)[a]	Melting points (°C)	
				Found	Lit [Ref]
7c	3-Nitrobenzaldehyde	30	87	168-170	168-172 [22]
7d	4-Methoxybenzaldehyde	20	90	205–207	205–208 [22]
7e	4-Cholorobenzaldehyde	25	92	185–187	184–185 [22]
7f	4-Methylbenzaldehyde	30	85	175–177	175–176 [22]

[a] Yields refer to the pure isolated products

129.2, 128.4, 128.0, 127.1, 125.2, 124.4, 121.6, 118.2, 117.7, 116.8, 111.2, 35.3, 21.0 ppm.

*13-(4-Methoxylphenyl)-indeno[1,2-b]naphtho[1,2-e]pyran-12(13H)-one(**5g**)*

Yellow solid; mp: 225–226 °C; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 7.87–7.82$ (m, 3H), 7.49 (d, $J = 9.2$ Hz, 1H), 7.43–7.27 (m, 6H), 7.23 (d, $J = 8.8$ Hz, 2H), 6.75 (d, $J = 8.8$ Hz, 2H), 5.58 (s, 1H), 3.71 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 192.5$, 167.0, 158.1, 148.9, 136.9, 136.1, 132.4, 132.2, 131.9, 131.8, 130.0, 129.5, 129.1, 128.4, 127.1, 125.2, 124.4, 121.6, 118.2, 117.7, 116.8, 113.9, 111.2, 55.1, 34.8 ppm.

Synthesis of 8,12-dihydro-8,10-dimethyl-12-(aryl)-7-oxa-8,10-diazabenzo[*a*]anthracene-9,11-dione(**6a–f**) and 9,10-dihydro-9,9-dimethyl-12-aryl-8*H*-benzo[*a*]xanthen-11(12*H*)-one(**7a–f**)

A stirred mixture of arylaldehydes (1 mmol), β-naphthol (1 mmol), and 1,3-dimethylbarbituric acid (**6a–f**) or dimedone (**7a–f**) (1 mmol) and H_3PO_4/Al_2O_3 (50 % w/w, 100 mg) was reacted in an oil bath at 120 °C for the appropriate times (Table 1). Completion of the reaction was indicated by TLC, after which it was cooled to room temperature and the crude solid product was dissolved in dichloromethane, and filtered for separation of the catalyst. The catalyst was washed twice with dichloromethane (2 × 5 ml), and then the recovered catalyst was dried in an oven at 100 °C for 3 h. The filtered organic solution was concentrated. The solid product was purified by recrystallization procedure in aqueous EtOH (15 %).

Select characterizations of the orange–red products are given below.

*8,12-Dihydro-8,10-dimethyl-12-(phenyl)-7-oxa-8,10-diazabenzo[a]anthracene-9,11-dione(**6a**)*

White solid; mp: 226–228 °C; ^{1}H NMR (400 MHz, CDCl3): $\delta = 7.96$ (d, $J = 7.8$ Hz, 1H), 7.85 (m, 2H), 7.46–7.35 (m, 5H), 7.23–7.10 (m, 3H), 5.81 (s, 1H), 3.61 (s, 3H), 3.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 161.9$, 152.2, 150.6, 147.1, 143.8, 131.7, 130.9, 129.4, 128.5, 128.4, 128.2, 127.4, 126.7, 125.4, 123.9, 117.4, 116.2, 91.4, 35.9, 29.0, 28.1. IR (KBr, cm^{-1}): 2,928, 1,706, 1,651, 1,485, 1,233, 1,179.

*8,12-Dihydro-8,10-dimethyl-12-(p-tolyl)-7-oxa-8,10-diazabenzo[a]anthracene-9,11-dione(**6b**)*

White solid; mp: 196–198 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.98$ (d, $J = 8.4$ Hz, 1H), 7.84–7.80 (m, 2H), 7.46–7.37 (m, 3H), 7.26 (d, $J = 7.5$ Hz, 2H), 7.02 (d, $J = 7.5$ Hz, 2H), 5.78 (s, 1H), 3.60 (s, 3H), 3.32 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 161.9$, 152.1, 150.6, 147.1, 140.9, 136.3, 131.7, 130.9, 129.3, 129.1, 128.4, 128.0, 127.3, 125.4, 123.9, 117.5, 116.2, 91.5, 35.5, 28.9, 28.1, 20.9. IR (KBr, cm^{-1}): 2,924, 1,700, 1,643, 1,487, 1,232, 1,179.

*8,12-Dihydro-8,10-dimethyl-12-(4-nitrophenyl)-7-oxa-8,10-diazabenzo[a]anthracene-9,11-dione(**6d**)*

White solid; mp: 288–290 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.07$ (d, $J = 8.4$ Hz, 2H), 7.91–7.79 (m, 3H), 7.56–7.42 (m, 5H), 5.90 (s, 1H), 3.63 (s, 3H), 3.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 161.7$, 152.4, 150.7, 150.4, 147.1, 146.5, 131.7, 130.4, 130.2, 129.2, 128.7, 127.8, 125.7, 123.7, 123.3, 116.3, 115.7, 89.9, 36.0, 29.1, 28.2. IR (KBr, cm^{-1}): 3,070, 2,924, 2,855, 1,709, 1,667, 1,596, 1,227, 1,175.

*8,12-Dihydro-8,10-dimethyl-12-(4-chlorophenyl)-7-oxa-8,10-diazabenzo[a]anthracene-9,11-dione(**6e**)*

White solid; mp: 270–272 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.88$–7.81 (m, 3H), 7.47–7.14 (m, 7H), 5.78 (s, 1H), 3.60 (s, 3H), 3.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 161.9$, 152.2, 150.5, 147.1, 142.3, 132.5, 131.7, 130.7, 129.7, 129.6, 128.5, 127.6, 125.6, 123.7, 116.7, 116.3, 90.9, 35.4, 29.1, 28.2. IR (KBr, cm^{-1}): 2,924, 2,855, 1,708, 1,671, 1,648, 1,225, 1,174, 1,081.

*9,10-Dihydro-9,9-dimethyl-12-phenyl-8H-benzo[a]xanthen-11(12H)-one(**7a**)*

White solid; mp: 151–153 °C; 1H NMR (400 MHz, $CDCl_3$): $\delta = 7.99$ (d, $J = 8.1$ Hz, 1H), 7.78–7.74 (m, 2H), 7.42–7.04 (m, 8H), 5.70 (s, 1H), 2.57 (s, 2H), 2.33 (d, $J = 16.2$ Hz, 1H), 2.26 (d, $J = 16.2$ Hz, 1H), 1.11 (s, 3H), 0.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 196.8$, 163.8, 147.7, 144.7, 131.4, 131.3, 128.7, 128.4, 128.3, 128.1, 126.9, 126.1, 124.8, 123.6, 117.6, 117.0, 114.2, 50.8, 41.3, 34.6, 32.2, 29.2, 27.1. IR (KBr, cm^{-1}): 3,055, 2,954, 2,884, 1,651, 1,374, 1,229, 1,178, 1,076, 811.

*9,10-Dihydro-9,9-dimethyl-12-(4-nitrophenyl)-8H-benzo[a]xanthen-11(12H)-one(**7b**)*

White solid; mp: 178–180 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.04$ (d, $J = 8.4$ Hz, 2H), 7.82–7.79 (m, 3H), 7.52–7.33 (m, 5H), 5.81 (s, 1H), 2.59 (s, 2H), 2.36 (d, $J = 16.2$ Hz, 1H), 2.26 (d, $J = 16.2$ Hz, 1H), 1.13 (s, 3H), 0.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 196.6$, 164.5, 151.8, 147.7, 146.2, 131.5, 130.9, 129.5, 129.3, 128.6, 127.3, 125.2, 123.5, 123.0, 117.0, 115.9, 112.9, 50.7, 41.3, 34.8, 32.2, 29.2, 27.0. IR (KBr, cm^{-1}): 3,077, 2,934, 1,645, 1,597, 1,516, 1,377, 1,343, 1,225, 1,177, 1,026, 827.

*9,10-Dihydro-9,9-dimethyl-12-(3-nitrophenyl)-8H-benzo[a]xanthen-11(12H)-one(**7c**)*

White solid; mp: 168–170 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.10$ (s, 1H), 7.95–7.80 (m, 5H), 7.47–7.35 (m, 4H), 5.81 (s, 1H), 2.61 (s, 2H), 2.36 (d, $J = 16.2$ Hz, 1H), 2.26 (d, $J = 16.2$ Hz, 1H), 1.13 (s, 3H), 0.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 196.7$, 164.5, 148.3, 147.7, 146.7, 134.7, 131.5, 130.9, 129.6, 129.0, 128.6, 127.3, 125.1, 123.1, 123.0, 121.5, 117.1, 115.9, 113.1, 50.7, 41.3, 34.7, 32.2, 29.2, 27.1. IR (KBr, cm^{-1}): 3,071, 2,955, 1,649, 1,528, 1,372, 1,356, 1,224, 1,172, 1,025, 809.

*9,10-Dihydro-9,9-dimethyl-12-(4-methoxyphenyl)-8H-benzo[a]xanthen-11(12H)-one(**7d**)*

Colorless crystals; mp: 181–182 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 1.91–2.08 (m, 2H), 2.31–2.48 (m, 2H), 2.57–2.76 (m, 2H), 3.69 (s, 3H), 5.69 (s, 1H), 6.71 (d, $J = 8.0$ Hz, 2H), 7.23–7.45 (m, 5H), 7.77 (t, $J = 8.4$ Hz, 2H), 7.96 (d, $J = 8.4$ Hz, 1H). IR (KBr, cm^{-1}): 2,945, 2,833, 1,651, 1,595, 1,460, 1,378, 1,251, 1,227, 1,188, 1,175, 1,130, 1,034, 952, 829, 748.

Results and discussions

Xanthenes and benzoxanthenes are important classes of biologically active heterocycles [9, 10] showing fluorescence activities [11], and are used in industrial applications and as precursors in the synthesis of heterocyclic compounds [12]. Also, these compounds have been shown to have antioxidant activity by 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging assay [13]. These compounds are being utilized as antagonists for paralyzing action of zoxazolamine and in photodynamic therapy. Xanthenes have also been employed as dyes and pH-sensitive fluorescent materials for visualization of biomolecules and in laser technologies [14]. Thus, the development of an environmentally benign methodology for the synthesis of benzoxanthene derivatives is in great demand. Here, we investigated the synthesis of various benzoxanthene pigments under catalytic amounts of H_3PO_4/Al_2O_3.

In the initial experiment, a test reaction using benzaldehyde (1 mmol), and dimedone (2 mmol) at 120 °C under solvent-free conditions and without any catalyst was performed in order to establish the effectiveness of the catalysts. The reaction in the absence of catalyst did not produce the desired product. The reaction in the presence of H_3PO_4/Al_2O_3 (50 % w/w) in different solvents did not complete (yield % = trace−50 % range) and starting materials were observed even after 24 h. The effects of the catalyst at different reaction temperatures (60, 80, 100, and 120 °C) and different amounts of catalyst (60, 80, 100, and 120 mg) were investigated. The best result was obtained by carrying out the reaction with 100 mg of H_3PO_4/Al_2O_3 (50 % w/w) at 120 °C under solvent-free conditions, because of the high yields of the product and short reaction times. Using optimized reaction conditions, the scope and efficiency of the reaction were explored for the synthesis of benzoxanthenes (Table 1). Thus, we examined the condensation of arylaldehydes (1 mmol) and dimedone (2 mmol) under the mentioned optimized conditions. The reaction proceeded efficiently with various kinds of aromatic aldehydes in good to excellent yields within short reaction times. Several structurally diverse aldehydes (Table 1) were subjected to condensation with dimedone under the catalytic influence of H_3PO_4/Al_2O_3 (50 % w/w) and thermal solvent-free conditions. 3,4,6,7-tetrahydro-3,3,6,6-tetramethyl-9-aryl-2*H*-xanthene-1,8(5*H*,9*H*)-diones (**1a–e**) were obtained in high yields.

In continuation of our ongoing research program, we found that H_3PO_4/Al_2O_3 is useful for the synthesis of 3,4-dihydro-3,3-dimethyl-12-aryl-2*H*-benzo[*b*]xanthene-1,6,11(12*H*)-triones (**2a–i**) by using of arylaldehydes, dimedone and 2-hydroxy-1,4-naphthoquinone. The three component reaction of arylaldehydes, *β*-naphthol and 2-hydroxy-1,4-naphthoquinone cause to prepare 14-aryl-14*H*-dibenzo [*a,i*]xanthene-8,13-diones (**3a–i**). The application of this protocol was extended to a variety of aromatic aldehydes. The reactions proceeded smoothly with different aldehydes substituted with electron-donating/electron-withdrawing groups giving excellent yields of the desired products. Interestingly halo-substituted aromatic aldehydes required shorter reaction times than their electron-rich counterparts. In this conditions, H_3PO_4/Al_2O_3 is able to efficiently catalyze the synthesis of 13-aryl-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraones (**4a–g**) from pseudo-three-component reaction of arylaldehydes (1 mmol), and 2-hydroxy-1,4-naphthoquinone (2 mmol). 13-Aryl-indeno[1,2-*b*]naphtha[1,2-*e*]pyran-12(13*H*)-ones (**5a–g**) were prepared from the condensation of *β*-naphthol (1 mmol), arylaldehydes (1 mmol), and 2*H*-indene-1,3-dione(1 mmol) utilizing H_3PO_4/Al_2O_3 under solvent-free conditions at 120 °C.

In order to broaden the scope of this protocol, we decided to synthesis 8,12-dihydro-8,10-dimethyl-12aryl-7-oxa-8,10-diazabenzo[*a*]anthracene-9,11-diones (**6a–f**) from the reaction of arylaldehydes (1 mmol), *β*-naphthol (1 mmol), and 1,3-dimethylbarbituric acid (1 mmol). Also, the successful condensation of aldehydes, *β*-naphthol and dimedone under similar conditions produced the 9,10-dihydro-9,9-dimethyl-12-aryl-8*H*-benzo[*a*]-xanthen-11(12*H*)-ones (**7a–f**).

Interestingly, a variety of aldehydes including *ortho*-, *meta*-, and *para*-substituted aryl aldehydes participated well in this reaction and gave the corresponding benzoxanthene derivatives in good to excellent yields without the formation of any by-products.

We also investigated the recycling of the catalyst under solvent-free conditions using a model reaction of benzaldehyde, *β*-naphthol, and 2-hydroxy-1,4-naphthoquinone. After completion of the reaction, the reaction mixture was cooled to room temperature, and the crude solid product was dissolved in dichloromethane. The mixture was filtered for separation of the catalyst. The catalyst was washed twice (2 × 5 ml) using dichloromethane. The recovered catalyst was dried in vacuo and

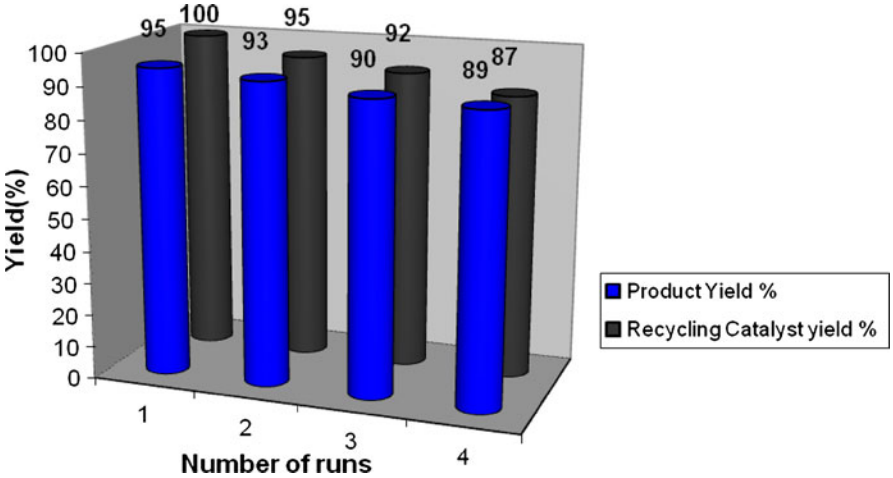


Fig. 1 Investigation of the recycling of H_3PO_4/Al_2O_3

was used for the subsequent catalytic runs (**3a**). The recovered catalyst was reused four times without any loss of its activities (Fig. 1).

Conclusion

We have developed a green and straightforward protocol for the synthesis of benzoxanthene derivatives using H_3PO_4/Al_2O_3(50 % w/w) as catalyst under thermal solvent-free conditions. This procedure provides several advantages such as cleaner reactions, easier work-up, reduced reaction times, reusable catalyst, and an eco-friendly promising strategy.

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