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1,3-Dibromo-5,5-dimethylhydantoin (DBH)/kaolin: An efficient reagent system for the synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes under solvent-free conditions

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Abstract

1,3-Dibromo-5,5-dimethylhydantoin, has been used as an efficient catalyst for the synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]-xanthenes in the presence of kaolin. All reactions are performed in the absence of solvent in relatively short reaction times in good to high yields.

Keywords: Kaolin; 1,3-Dibromo-5,5-dimethylhydantoin; Xanthene derivatives; Solvent-free conditions

The xanthene derivatives, especially benzoxanthenes, have wide range of biological and therapeutic properties [1–5]. Furthermore, due to their useful spectroscopic properties, they were used as dyes [6], in laser technologies [7], and in fluorescent materials for visualization of biomolecule [8]. Many procedures describe the synthesis of xanthenes and benzoxanthenes including cyclodehydrations [9–13]. In addition, 14*H*-dibenzo[*a*,*j*]xanthenes and related products were prepared by reaction of 2-naphthol with formamide [14], 2-naphthol-1-methanol [15], carbon monoxide [16] and sulfomic acid [17]. Even though various procedures were reported, disadvantages including low yields, prolonged reaction times, use of an excess of reagents/catalysts and use of toxic organic solvents necessitate the development of an alternative route for the synthesis of xanthene derivatives.

Kaolin is natural substance that obtained from clay. With abilities to act as good as ceramic material; (no toxicity, ability to withstand extreme heat and pressure) it is believed that kaolin has tremendous potential to be utilized as solid support material in both laboratory scale and industrial scale. Currently, strong interests in such natural supports were due to eco-friendly demands in many modern industrial applications [18]. Kaolin, montmorillonite K10 and KSF supported with transition metal chlorides were employed to esterify *tert*-butanol with acetic anhydride to *tert*-butyl acetate with more than 98% selectivity. A noteworthy feature was the low activity of the catalysts for the dehydration of *tert*-butanol below 50 °C [19]. Thermally activated Nigerian Ukpor kaolinite clay and Udi clay were shown to be

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good catalysts for the preparation of *n*-propyl acetate [20]. Brazilian kaolinite intercalated with a porphyrin derivative catalyzed Baeyer–Villiger oxidation of cyclohexanone to ε-caprolactam by hydrogen peroxide. In the presence of the same catalyst iodosylbenzene brings about the epoxidation of cyclooctene and oxidation of cylcohexane to cyclohexanone [21]. Acid-treated clay (K10, bentonite, or kaolin) catalyzed the triazenes formation by diazotization ofaryl amines followed by addition of a cyclic secondary amine [22].

1. Experimental

All chemicals were purchased from Merck or Fluka Chemical Companies. All known compounds were identified by comparison of their melting points and spectral data with those reported in the literature. Progress of the reactions was monitored by thin layer chromatography (TLC) using silica gel SIL G/UV 254 plates. Melting points were determined on an electrothermal type 9200 melting point apparatus. IR spectra were recorded using a Shimadzu IR-470 spectrometer with KBr plates. ^{1}H NMR spectra were recorded on a Bruker Avance-400 MHz spectrometer.

At first, a mixture of arylaldehyde (1 mmol), kaolin (100 mg) and DBH (0.1 mmol) was stirred and heated on the oil bath at 125 °C for 1 min. Then 2-naphthol (2 mmol) was added to the mixture. The resulting mixture was stirred vigorously for an appropriate period of time, as mentioned in Table 1. The progress of the reaction was followed by TLC (*n*-hexane:ethyl acetate, 8:2). After completion of the reaction, the reaction mixture was diluted with dichloromethane (3 mL) and kaolin was filtrated. The solvent was evaporated under vacuum and the resulting solid products were recrystallized from ethanol. The products were found to be pure and no further purification was necessary.

1.1. Spectral data of the selected compounds

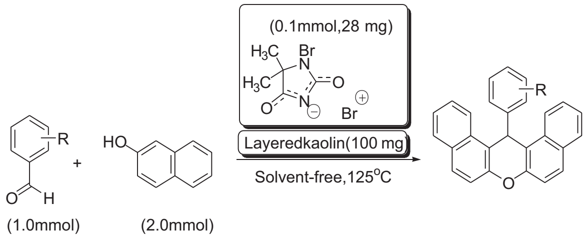
14-(Phenyl)-14H-dibenzo[a,j]xanthene: Colorless crystals; mp 184–185 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 6.46 (s, 1H, CH), 6.96 (t, 1H, J = 7.2 Hz, ArH), 7.12 (t, 2H, J = 7.2 Hz, ArH), 7.36–7.58 (m, 8H, ArH), 7.74–7.81 (m, 4H, ArH), 8.37 (d, 2H, J = 8.4 Hz, ArH); IR (KBr, cm^{-1}): 3070, 3020, 1620, 1590, 1430, 1400, 1250, 1150, 1075, 825, 740.

14-(4-Methylphenyl)-14H-dibenzo[a,j]xanthenes: Colorless crystals; mp 224–225 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 2.11 (s, 3H, CH$_3$), 6.43 (s, 1H, CH), 6.93 (d, 2H, J = 7.8 Hz, ArH), 7.22–7.36 (m, 8H, ArH), 7.42–7.81 (m, 4H, ArH), 8.37 (d, 2H, J = 8.4 Hz, ArH); IR (KBr, cm^{-1}): 3068, 3022, 1620, 1590, 1512, 1395, 1248, 1110, 810, 740.

14-(3-Nitrophenyl)-14H-dibenzo[a,j]xanthenes: Yellow crystals; mp 207–208 °C; ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.52 (s, 1H), 7.10–8.56 (m, 16H); IR (KBr, cm^{-1}): 3060, 1595, 1525, 1350, 1240, 1140, 810, 750.

2. Results and discussion

In 2011, Ghasemnejad-Bosra *et al.* reported that 1,3-dibromo-5,5-dimethylhydantoin (DBH) (0.12 mmol, 34 mg) is able to efficiently catalyze the synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes (48–61 min, 90–96%) [23]. Based on this study and in continuation of our ongoing research program on the development of new methods for the organic transformations [24,25], we have found that when the same reaction is carried out in the presence of kaolin, in addition to decreasing of the reaction time (3–40 min), the procedure became more easier (It should be noted that in the absence of kaolin, the mixture became very sticky, which causes the difficulty in the mixing of the reactants). Optimization of the reaction conditions showed that the best results can be obtained under the conditions presented in Scheme 1.

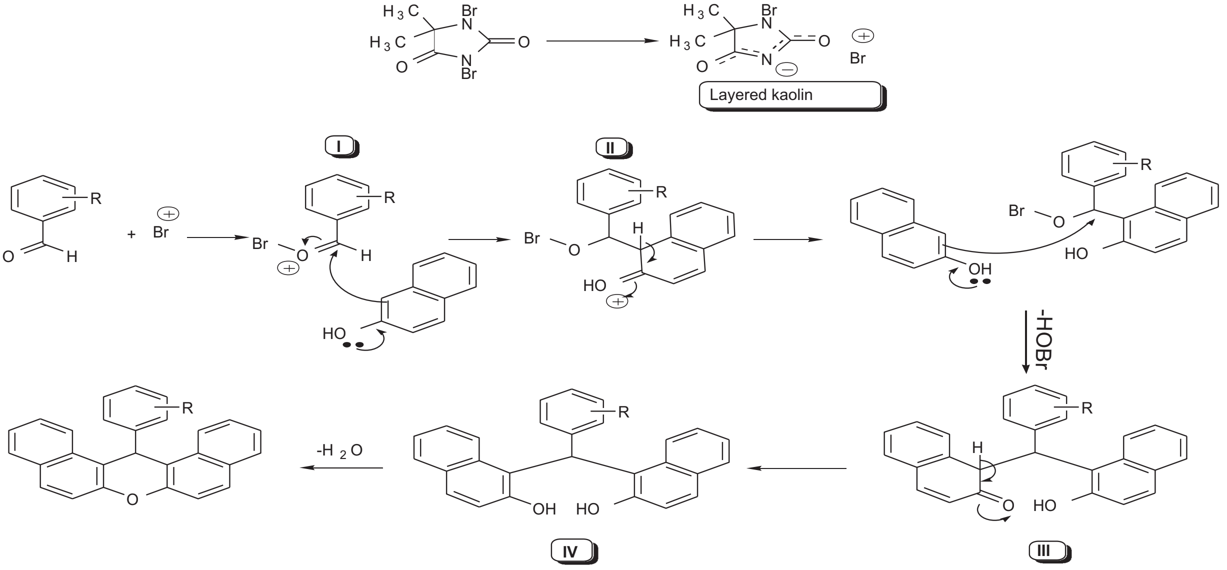


Scheme 1. Preparation of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes.

Table 1
Kaolin/DBH catalyzed synthesis of xanthene derivatives.[a]

Entry	R	Time (min)	Yield (%)[b]	Mp (°C)	
				Found	Reported
1	C_6H_5–	30	85	184–185	181–183
2	3-CH_3–C_6H_4–	35	83	197–198	198
3	4-CH_3–C_6H_4–	40	81	224–225	226–228
4	4-F–C_6H_4–	9	90	236–237	236
5	2-Cl–C_6H_4–	10	85	213–215	213–215
6	3-Cl–C_6H_4–	25	86	208–210	209–210
7	4-Cl–C_6H_4–	5	91	287–288	289–290
8	3-Br–C_6H_4–	15	89	190–191	190–191
9	4-Br–C_6H_4–	6	87	291–293	296
10	3-NO_2–C_6H_4–	9	90	207–208	210–211
11	4-NO_2–C_6H_4–	3	95	314–315	310–312
12	4-CN–C_6H_4–	12	87	289–291	293–295
13	Cinnammaldehyde	–	–[c]	–	–
14	Valeraldehyde	–	–[c]	–	–

[a] Products were characterized by ^{1}H NMR, IR and melting point and also by comparison with the reported in literature data [9,17,26–32].
[b] Isolated yields.
[c] Mixture of products.



Scheme 2. Proposed mechanism.

After optimization of the reaction conditions different types of aromatic aldehydes were subjected to the requested reaction under the determined conditions. As shown in Table 1, aryl-aldehydes were converted into their benzoxanthene derivatives in good to high isolated yields (Table 1, 81–95%), although the reaction times were significantly affected by the electron-withdrawing and releasing substituents on the benzene ring. The electron-withdrawing substituted benzaldehydes reacted very well and produced corresponding 14-aryl-14*H*-dibenzo[*a*,*j*]-xanthenes in good to excellent yields in shorter times than arylaldehydes with electron-donating groups. Because of the formation of the mixture of products, the method is not useful for the preparation of xanthenes derivatives from aliphatic and double bond containing aldehydes (Table 1, entries 13, 14).

Although the actual mechanism of the reaction is unclear, a reasonable explanation due to the high catalytic activity of DBH and mechanistic operation of DBH in similar reactions [33] is shown in Scheme 2. On the basis of this mechanism, 1,3-dibromo-5,5-dimehtylhydantion produces the bromonium cation (Br^+) and activates the carbonyl group by the formation of oxygen cation **I**. The reaction follows by the nucleophilic attack of 2-naphthol on the activated carbonyl of **I** to afford **II** which is *O*-activated by Br^+. Then the second 2-naphthol attacks on **II** to generate **III**. In the last step, the corresponding 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes is produced from **IV** by releasing H_2O. It is important to note that in the absence of kaolin a trace amount of the product is produced during a long reaction time. This result shows that kaolin may have the following roles for the promotion of the reaction: (i) a support for placing the reactants and catalyst closer together, and (ii) a support for adsorption of the produced water (Scheme 2).

In conclusion, we have demonstrated a mild and efficient protocol for the preparation of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes using kaolin/DBH reagent system. Short reaction times, easy work-up, and high yields of products are noteworthy advantages of this protocol. Furthermore, the use of an inexpensive, approximately non-toxic, commercially available, and highly efficient catalyst under solvent-free conditions makes the current method economically acceptable and industrially applicable. We have also proposed a plausible mechanism for the present reaction. The present methodology also has several other advantages such as: high reaction rates and excellent yields, no side reactions, ease of preparation and handling of the catalyst, cost efficiency of the catalyst and simple experimental procedure.

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