Synthesis, characterization and catalytic activity of titanium dodecylamino phosphate for synthesis of tetrahydrobenzo[a]xanthen-11-ones

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Synthesis, characterization and catalytic activity of titanium dodecylamino phosphate for synthesis of tetrahydrobenzo[a]xanthen-11-ones

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Titanium dodecylamino phosphate catalyst has been synthesized and characterized by various techniques. Titanium dodecylamino phosphate efficiently catalyses tetrahydrobenzo[a]xanthen-11-ones synthesis at room temperature and the products are formed in high yields. An equal molar mixture of methanol and water is found to be a suitable solvent. The catalyst can be recycled. Influence of various reaction parameters such as various solvents, catalyst dosage, effect of substituents on aldehydes and reusability have been studied. A plausible mechanism on its synthesis is proposed.

Keywords: Catalysts, Titanium dodecylamino phosphate, Xanthenes, Benzoxanthenes, Tetrahydrobenzo[a]xanthen-11-ones

Xanthenes and benzoxanthenes are important biological heterocycles possess therapeutic properties such as anti-viral, anti-inflammatory and anti-bacterial activities[1]. They act as antagonists for drug resistant leukemia and also for paralyzing the action of zoxazolamine[2]. These compounds have also found applications in dyes, laser technologies, *p*H sensitive fluorescent materials for visualization of biomolecules[3] and in photodynamic therapy. They have been used as rigid carbon skeletons for the construction of new chiral bidentate phosphine ligands with potential applications in catalytic processes. Many benzoxanthene derivatives are potent nonpeptidic inhibitors of recombinant human calpain I and novel CCR1 receptor antagonists[4, 5]. In addition, the xanthene skeleton is an important building block in a number of natural products[6] and has been used as versatile synthons because of the pyran ring.

Among the xanthene-based compounds, tetrahydrobenzo[a]xanthen-11-ones are of interest and have great potential for further synthetic transformations[7-11]. Catalysts such as ceric ammonium nitrate[12], proline triflate[13], $NaHSO_4.SiO_2$[14], strontium triflate[15], $Zr(HSO_4)_4$[16], dodecatungstophosphoric acid[17], iodine[18], $InCl_3/P_2O_5$[19], *p*-toluenesulfonic acid/ionic liquid ([bmim]BF_4)[20], $RuCl_4$[21], bronsted ionic liquid[22], molecular iodine[23] and trichloroacetic acid[24] have been employed for their synthesis. Many of these methods are unsatisfactory as they involve the use of halogenated solvents, catalyst loadings of up to 30 mol%, low yields, drastic reaction conditions, prolonged reaction times and tedious isolation procedures. All of these disadvantages led to further improvements toward the synthesis of new catalysts. Recently synthetic methods involve tetra-*n*-butyl-ammonium fluoride (TBAF) [25] and proline triflate[26] in water have been reported. However, the major problems associated with these routes are the need for refluxing conditions and longer reaction times. Therefore, it was thought worthwhile to develop a more convenient method for preparation of tetrahydrobenzo[a]xanthen-11-ones.

Mesoporous materials such as MCM-41, silica based organic-inorganic hybrid materials, non-siliceous mesoporous metal oxides, phosphates and organic polymers have been studied intensively due to their versatile applications[27]. Among the mesoporous materials, phosphates are efficient in several industrial important acid based reactions[28]. Presence of phosphate in mesoporous materials seems to enhance catalytic properties, stabilize surface area and crystal phase, improve the surface acidity and make the material porous. Metal phosphates are of interest because of their practical application in areas such as catalysis, ion exchange, intercalation chemistry and proton conduction[29]. Research on metal phosphates has led to the discovery of mesoporous aluminophosphates, nickel phosphate, iron phosphate, tin phosphate, zirconium phosphate and titanium phosphate[30]. Among the phosphates, titanium phosphates possess a broad range of applications such as ion exchange, intercalation, catalysts for liquid phase oxidations and photoreactions, non-linear optics and ionic conductivity[31]. The incorporation of phosphate ions in titania enhances important catalytic properties like stabilisation of surface area, crystal phase, and improvement in surface acidity[32]. As a transition metal ion oxide, titania possesses a unique type of surface involving acidic, basic and redox sites. It is an excellent solid acid catalyst in epoxidations, oxidative dehydrogenations and hydrogenations. In addition to high thermal stability, its amphoteric character makes titania a promising catalytic material.

Application of titania based catalyst in organic synthesis such as synthesis of bis(indolyl)methanes[33], dispiroacenaphthenone/oxindole pyrroloisoquinoline ring systems[34] and 3,4-dihydropyrimidin-2-(1*h*)-ones[35] have been reported. To the best of our knowledge there are no reports regarding the application of titania based catalyst in the synthesis of tetrahydrobenzo[a]xanthen-11-ones. Herein we report the instantaneous, solvent-free synthesis of a novel open framework titanium dodecylamino phosphate and its characterization by various physicochemical techniques. The catalytic activity of the present material towards the cost effective synthesis of tetrahydrobenzo[a]xanthen-11-ones has been investigated. The effects of various parameters such as effect of different solvents, catalyst dosage and reusability of the catalyst are also reported.

Experimental

Titanium tetraisopropoxide (Sigma Aldrich, 98%), dodecylamine (Sigma Aldrich, 98%) and orthophosphoric acid (Merck, 85 %) were obtained. Aldehydes were purchased from (Sisco Research Laboratories) and dimedone from (Oakwood Chemical Laboratories, USA). All the chemicals were of analytical reagent grade and were used without any further purification.

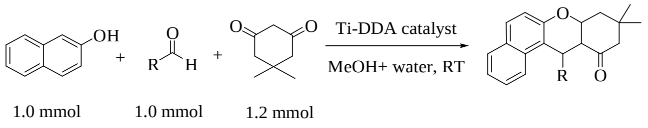
The synthesis of titanium dodecylamino phosphate was carried out at room temperature reported elsewhere[36].Typically, a calculated quantity of orthophosphoric acid (1 *M*) was added to titanium tetraisopropoxide (0.01 *M*) and stirred. To this well stirred mixture, dodecylamine (4 *M*) was added instantly and stirred vigorously to get a solid product. The product obtained was ground well, washed with ether and dried at 40 °C for about 30 min.

Qualitative phase analysis of titanium dodecylamino phosphate was studied using a Bruker AXS D8 Advance diffractometer at room temperature with Cu-Kα as the X-ray source of wavelength 1.5406 Å using Si (Li) PSD detector. The morphology of the material was investigated by scanning electron microscopy (SEM) with a Jeol (model JSM-6390LV) scanning electron microscope. Fourier transform infrared spectroscopy (FT-IR) was recorded on Thermo Nicolet (Avatar 370) spectrophotometer equipped with a pyroelectric detector (DTGS type) with a resolution of 4 cm^{-1} and provided with KBr beam splitter. Dispersive Raman spectrum was recorded on Bruker senterra instrument at a wavelength of 532 nm using laser radiation as source. The coordination and oxidation state of titanium in titanium dodecylamino phosphate was examined with diffuse reflectance UV-visible spectra (UV-vis DRS) recorded on a Varian spectrophotometer (Cary 5000) in the wavelength range of 175–800 nm. The ^{31}P magic-angle spin ing (MAS) NMR spectra was recorded at room temperature on a Bruker DRX-500 AV-III 500(S) spectrometer, at a spinning rate of 10–12 KHz, operating at 121.49 MHz using a 5 mm dual probe. The ^{13}C cross-polarization magic-angle spinning (CP-MAS) NMR spectra were recorded at room temperature on a DSX-300 Avance-III 400(L) NMR spectrometer at a spinning rate of 10–12 KHz operating at 75.47 MHz using a 5 mm dual probe.

To prepare the tetrahydrobenzo[a]xanthen-11-ones, a mixture of aromatic aldehyde (1.0 mmol), β-naphthol (1.0 mmol), 5,5-dimethylcyclohexane-1,3-dione (1.2 mmol) and titanium dodecylamino phosphate (0.05 g) in methanol:water (1:1) was magnetically stirred in a round bottom flask (Scheme 1). The progress of the reaction was monitored by TLC using chloroform:ethyl acetate (7:3) as the solvent system. Upon completion of the reaction, water (20 mL) was added to the mixture to remove unreacted reactants and the product was extracted with ethyl acetate (40 mL). The organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated under vacuum. The residue obtained was purified by column chromatography on silica gel to afford the pure products. Finally, the products were recrystallized from methanol.

Results and discussion

Figure 1 shows the powder X-ray diffraction pattern of titanium dodecylamino phosphate. Titanium dodecylamino phosphate exhibits peaks at



R = C_6H_5; 4-ClC_6H_4; 4-$NO_2C_6H_4$; 4-OHC_6H_4; 4-BrC_6H_4; 4-MeC_6H_4; 4-FC_6H_4.

Synthesis of tetrahydrobenzo[a]xanthen-11-ones catalyzed by titanium dodecylamino phosphate catalyst

Scheme 1

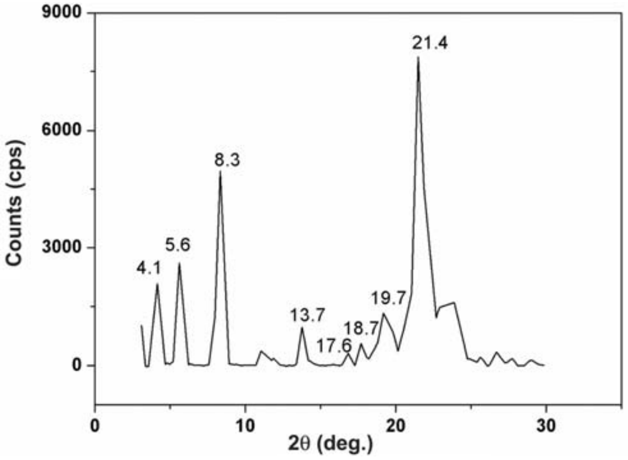


Fig. 1 – Powder X-ray diffraction pattern of titanium dodecylamino phosphate.

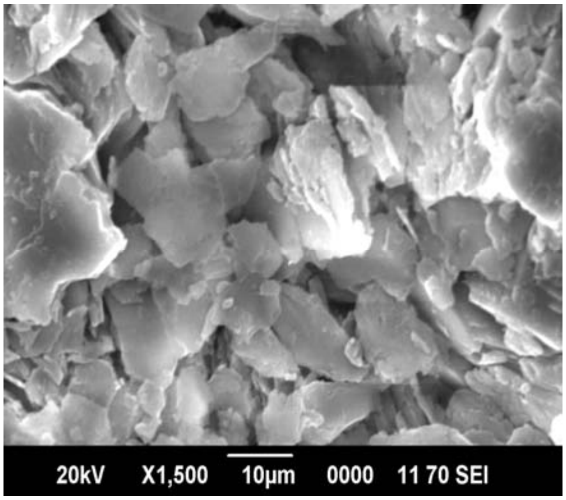
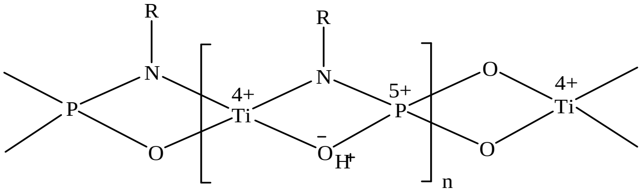


Fig. 2 – Scanning electron micrograph of titanium dodecylamino phosphate.



R = dodecyl

Fig. 3 – Proposed structure for titanium dodecylamino phosphate.

the 2θ of 4.1°, 5.6°, 8.3°, 13.7°, 17.6°, 18.7°, 19.7° and 21.4° with corresponding ***d***-spacings (Å) of 21.2, 15.6, 10.6, 6.4, 5.0, 4.7, 4.4 and 4.3. The pattern exhibits low angle diffraction peak at 4.1° characteristic of mesoporous structure. The peaks at 2θ of 18.7°, 13.7°, 8.0°, and 5.4° correspond to presence of –Ti–O– with a mesoporous structure[37-39]. The average crystallite size of the titanium dodecylamino phosphate was calculated in accordance with Scherer's equation, $D = K\lambda/\beta\cos\theta$, where D is the crystallite size, λ is the wavelength of the X-ray radiation (1.5406 Å), K the Scherer constant (= 0.9), β is the full width at half maximum (FWHM) of the diffraction peak measured at 2θ and θ is the diffraction angle. The average crystallite size of titanium image (Fig. 2) of titanium dodecylamino phosphate shows that the particles are in irregular flakes shaped in the entire sample.

The FT-IR spectrum of titanium dodecylamino phosphate (Supplementary data, Fig. S1) shows peak at 1639 cm^{-1}, corresponding to the bending vibration of –O–H bond[40]. The peak at 2920 cm^{-1} corresponds to the stretching vibrations of methylinic groups adsorbed on the surface of the titania[41]. The vibration around 1480–1450 cm^{-1} and 740–710 cm^{-1} correspond to scissoring and rocking modes of methylene group[42]. The band at 1558 cm^{-1} corresponds to the presence of –P–NH vibrations in titanium dodecylamino phosphate[43]. The peak at 1085 cm^{-1} is characteristic of vibration of the –P–O – bond of phosphate ions coordinated to Ti[44]. The peak at 964 cm^{-1} is characteristic of symmetric vibration of –P–O– moiety[45]. The peak in the range of 653–550 cm^{-1} corresponds to the framework bonds of –Ti–O– stretching vibration and confirms the presence of Ti in the titanium dodecylamino phosphate[46]. The material was found to be lamellar, possessing an open framework structure, with alternate arrangement of titania and phosphate tetrahedral, bonded through amine linkages (Fig. 3). The Raman spectrum of titanium dodecylamino phosphate shows peak at 1290 cm^{-1} and a small peak at 1060 cm^{-1} corresponds to antisymmetric and symmetric stretching modes of phosphate tetrahedra[47] (Fig. 4).

The UV-visible diffuse reflectance spectrum of titanium dodecylamino phosphate shows a strong peak at 215 nm due to the charge transfer transitions between empty 3***d***-orbital's of Ti(IV) cations and 2***p***-orbitals of oxygen anions (O2-) (Supplementary data, Fig. S2). The charge transfer transition infers the presence of titanium in tetrahedral coordination. A similar high energy absorption edge at 340 nm is assigned to the presence of titanium in tetrahedral coordination.

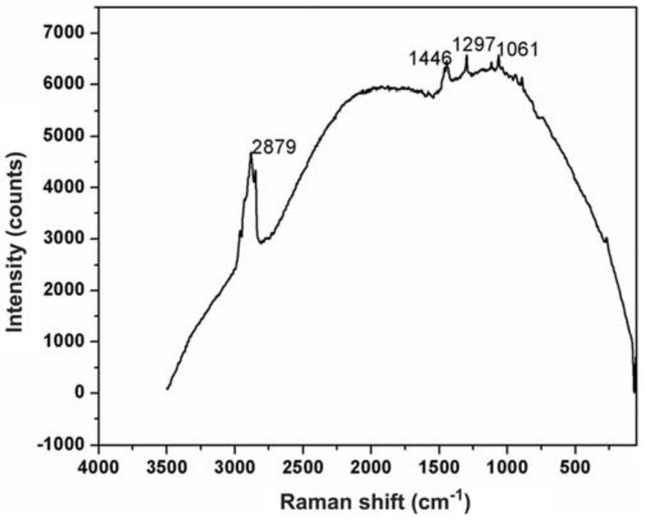


Fig. 4 – Dispersive Raman spectrum of titanium dodecylamino phosphate.

The ^{31}P MASNMR spectrum of titanium dodecylamino phosphate shows a sharp signal at 1.924 ppm with its spinning side bands (Supplementary data, Fig. S3). The ^{31}P resonance explains the presence of mesoporous crystalline titanium phosphate framework[48] which was observed in the range of –5 to 3 ppm. The presence of only one resonance clearly indicates that there is only one type of chemical environment of the phosphorus atoms. The ^{13}C CPMASNMR spectrum of titanium dodecylamino phosphate shows chemical shifts at 25 and 33 ppm corresponding to $(–CH_2)_{10}$, and $–CH_2NH^+_3$ groups respectively (Supplementary data, Fig. S4). The interior methylene carbons of alkyl chains are in trans conformation. The peak at 14 ppm is due to the terminal $–CH_3$ group of dodecylamine[49]. Peaks at 42.8 and 39.4 ppm may be assigned to the carbon (C_1) adjacent to the amine head group and the carbon (C_2) next to it respectively. The signal at 163.3 ppm corresponds to the amino group located near to phosphate. The signal also suggests that amino groups are intermediate between free and protonated form respectively[50].

To explore the efficacy of the catalyst (Table 1) and the optimum conditions required for the reaction, we investigated the multicomponent reaction of β-naphthol (1.0 mmol), benzaldehyde (1.0 mmol) and 5,5-dimethylcyclohexane-1,3-dione (1.2 mmol) in the absence of solvent and without any catalyst at room temperature (see Supplementary data, Table S1). It was found that about 14% yield was obtained after 4 h. The same reaction was performed in the presence of titanium dodecylamino phosphate catalyst (0.05 g) under solvent-free conditions. The time taken for reaction to obtain slight yield is found to be 120–180 min.

Table 1 – Synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo-[*a*]xanthene-11-ones with different solvents in the presence of TNDDAP catalyst. [React. cond.: benzaldehyde = 1.0 mmol; Dimedone = 1.2 mmol; Solvent = 5.0 mL; 2-Naphthol = 1.0 mmol; Temp. = RT; TNDDAP dosage = 100 mg]

Solvent	Time (h)	Yield (%)
Methanol	1.0	70
Acetonitrile	3.0	50
Chloroform	6.0	53
Methanol:Water	1.0	87
Ethanol	2.0	65
Water	-	No reaction
Tetrahydrofuran	-	No reaction

As solubility is an important criteria for organic reactions to carry out, we have attempted the reaction in various solvents having different polarity. Acetonitrile and chloroform afforded low yields while in water and tetrahydrofuran no reaction was detected. 14-Aryl-14H-dibenzo[a, j]xanthenes was obtained as a by-product by refluxing in dichloromethane. Finally when methanol or methanol:water (1:1) was used, the yield has been increased to 85% better than any other solvents examined. It was found that the reaction in methanol or methanol:water proceeds smoothlybut with moderate yield. Interestingly, when titanium dodecylamino phosphate (0.05 g) was used in presence of methanol:water (1:1) at room temperature, the reaction proceeds smoothly in a short reaction time and afforded maximum yield of the product (Table 1). The results show that the catalytic performance is strongly affected by the solvents (methanol or methanol:water). As protic solvents, methanol and water will solubilize dimedone and bring the reactants on the surface of the catalyst and thus enhance the yield. In comparison with other solvents, the combination of methanol and water gave products with higher yields and were found to be more suitable for the reaction to yield pure tetrahydrobenzo[a]xanthen-11-ones at room temperature[51].

In order to evaluate the catalytic activity of titanium dodecylamino phosphate, the catalytic activity of the reaction with other catalysts such as $TiCl_4$ and TiO_2 (Degussa) were compared. However, titanium dodecylamino phosphate was found to be most effective with respect to reaction time as well as yield of the product. It is proposed that the halogens in $TiCl_4$, interfere with the substrate and yields by-products

Table 2 – Effect of catalyst dosage on the catalytic activity of TNDDAP catalyst. [React. cond.: Benzaldehyde = 1.0 mmol; Dimedone = 1.2 mmol; 2-Naphthol = 1.0 mmol; Methanol: Water = 5.0 mL; Temp. = RT]

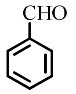
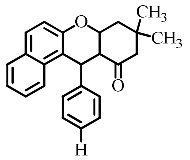
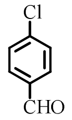
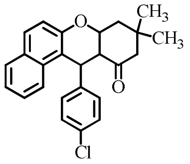
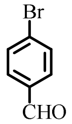
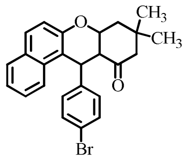
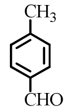
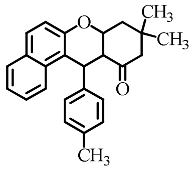
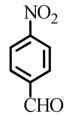
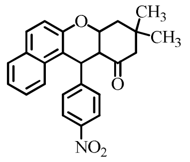
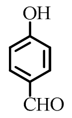
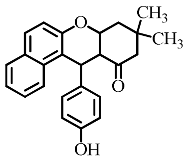
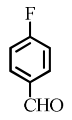
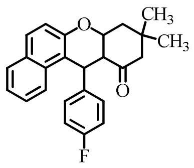
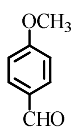
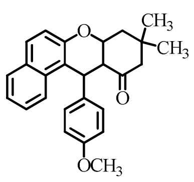
Amt of catalyst (mg)	Time (h)	Yield (%)
30	1.6	60
50	1.3	69
70	0.7	72
100	1.0	87

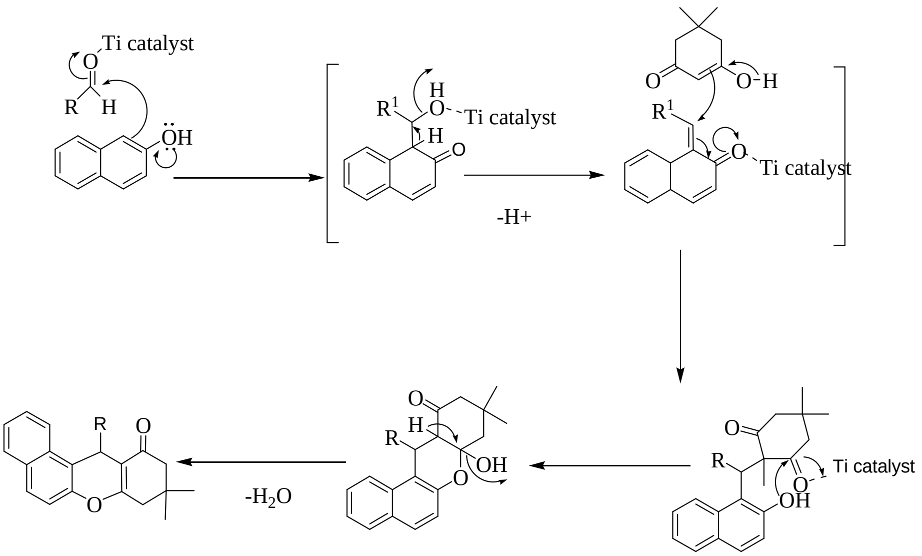
in larger amounts, which in turn affords lower yield of the product at room temperature with methanol:water (1:1) as solvent. TiO_2 (Degussa) yields 70% product in 90 min. Compared to TiO_2, titanium dodecylamino phosphate was found to be a more promising catalyst for the reaction. To optimize the amount of catalyst, the reaction was investigated with varying amounts of catalyst (0.03–0.1 g) (Table 2); a change in reaction time as well as yield was observed. The optimum amount of catalyst was found to be 0.10 g with respect to product yield and amount of catalyst. Further increase in the amount does not affect the yield significantly. Incorporation of titanium ions and amine in phosphate framework may be responsible for enhanced activity toward the synthesis of tetrahydrobenzoxanthen-11-ones.

Encouraged by the above results the protocol was extended to various aromatic aldehydes using titanium dodecylamino phosphate (0.05 g) in methanol: water (1:1). Aromatic aldehydes substituted with electron withdrawing and electron donating substituents show equal ease toward the product formation in good to high yields. However, *para* substituted aldehydes gave better results as compared to the *ortho* substituents (as conversion is negligible, data not given here) due to steric hindrance associated with *ortho* substituents. The results obtained in the present method are illustrated in (Table 3). It is also concluded that the aldehydes bearing electron withdrawing groups facilitate the reaction and afford higher yields in shorter reaction times. The NMR data of the compounds are given as Supplementary data (Table S2).

The reusability of the catalyst was examined by treating benzaldehyde (1.0 mmol) with 5,5-dimethyl-cyclohexane-1,3-dione (1.2 mmol) and β-naphthol (1.0 mmol) in the presence of titanium dodecylamino phosphate (0.10 g). The reaction proceeds smoothly with slight increase in reaction time and furnished the product in 60–80% yield. The results reveal that the catalyst is reusable up to three cycles without any appreciable loss in its catalytic activity. At the end

Table 3 – Synthesis of 12-aryl-8,9,10,12-tetrahydro-benzo-[*a*]xanthene-11-ones with substituted aromatic aldehydes in presence of TNDDAP catalyst. [React. cond.: Aromatic aldehyde = 1.0 mmol; Dimedone = 1.2 mmol; 2-Naphthol = 1.0 mmol; Methanol:Water = 5.0 mL; Temp. = RT; TNDDAP = 100 mg]

Reactant	Product	Time (h)/ Yield (%)/ M. pt. (°C)
		1.0 87 148-151
		2.0 85 178-179
		2.0 86 185-187
		3.0 89 175-176
		2.5 90 175-178
		3.5 88 223-225
		2.5 85 188-190
		3.5 80 201-203



Plausible reaction mechanism for the formation of tetrahydrobenzo[a]xanthen-11-ones

Scheme 2

of the reaction, the catalyst was filtered, washed with diethyl ether dried at room temperature and reused in another reaction.

A tentative mechanism for the formation of tetrahydrobenzo[a]xanthen-11-ones is proposed in Scheme 2. We propose that the reaction may have proceeded via *ortho*-quinone methide intermediate, which is formed by the nucleophilic addition of β-naphthol to aldehyde, catalyzed by titanium dodecylamino phosphate[52]. Subsequent substitution of the oxygen atom, coordinated by titanium dodecylamino phosphate with 5,5-dimethyl-1,3-cyclohexanedione and elimination of water molecule affords the desired product.

In the present study, the titanium dodecylamino phosphate catalyst was prepared and characterized by various physicochemical techniques. Powder XRD data shows the presence of –Ti–O– framework structure in the material. The infrared and Raman spectra present peaks due to vibrations of Ti–O, P–O and O–H bonds. UV-vis diffuse reflectance reveals the tetrahedral coordination of Ti in the framework. The ^{31}P MASNMR spectrum suggests the existence of titanium phosphate framework topology, while the ^{13}C NMR suggests the presence of amino group near the phosphate framework. Study of the catalytic application of the material towards tetrahydrobenzoxanthen-11-ones synthesis shows several advantages such as catalyst reusability, high yields of product, short reaction times, inexpensive and ready availability of the catalyst, making the procedure an alternate method to the existing methods. The reaction parameters such as solvents, amounts of catalyst and aldehydes on tetrahydrobenzoxanthen-11-ones synthesis have been investigated.

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