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Metal Free Visible Light Driven Oxidation of Alcohols to Carbonyl Derivatives Using 3, 6-Di(pyridin-2-yl)-1,2,4,5-tetrazine (pytz) as Catalyst[†]

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3, 6-di(pyridin-2-yl)-1,2,4,5-tetrazine (pytz) catalyzed oxidation of alcohols to corresponding carbonyl compounds under visible light irradiation is described. This reaction occurs smoothly at room temperature and shows good tolerance of functional groups. It provides an alternative approach for the synthesis of alkyl and aryl aldehydes and ketones.

Introduction

Recently, organic reactions driven by visible light at ambient temperature in presence of dyes has attracted much interest of synthetic chemists. Usually, polypyridine complexes of ruthenium and iridium have been utilized as dyes in most of these reactions.[1] More recently, few organic dyes have also been reported as visible light photoredox catalysts.[2]

Among organic transformations, the selective oxidation of alcohols to the corresponding carbonyl groups is one of the most important and widely utilized in the manufacture of fine chemicals and intermediates.[3] Consequently, several effective reagents and methods have been developed, including stoichiometric oxidizing agents such as hypochlorite,[4] chromium based reagents,[5] active manganese oxides and permanganate,[6,7] Dess-Martin periodinane,[8] o-iodoxybenzoic acid (IBX),[9] ruthenium based reagents,[10] osmium(VIII) oxide[11] and activated DMSO in Swern oxidation.[12] However, most of these reagents are toxic, hazardous and sometimes generates harmful wastes. Numerous homogenous as well as heterogeneous transition metal[13-19] and TEMPO[20] based catalysts have also been reported to be active for aerobic oxidation of alcohols, as they are particularly advantageous from environmental and economic perspective. However, they require relatively expensive metal catalysts, a large amount of additives, and higher temperature to obtain satisfactory results. Few reports also appeared on photocatalytic conversion of alcohols to aldehydes and ketones using visible

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light.[2i,21] Due to the importance of this reaction, the development of efficient, mild, and metal free safe oxidation processes are still highly desirable.

Recently, we have reported the visible light absorption and reversible one-electron reduction properties of the 3, 6-di(pyridin-2-yl)-1,2,4,5-tetrazine (pytz) molecule (Figure 1)[2b] and its application to the photocatalytic synthesis of 2-substituted benzimidazoles and benzothiazoles from different aldehydes. s-Tetrazines (Tz) are known to have a strong electron-deficient character and accept electrons and protons
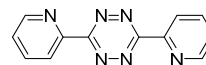

Fig. 1 3, 6-di(pyridin-2-yl)-1,2,4,5-tetrazine (pytz).

simultaneously to form dihydrotetrazenes (H$_2$Tz) via anion radical (Scheme 1).[22] This reducing nature of the s-tetrazines is even more prominent for the first excited state, which therefore has a relatively strong oxidizing power.[22] Consequently, s-tetrazines interact with various electron donor substrates at an excited state.
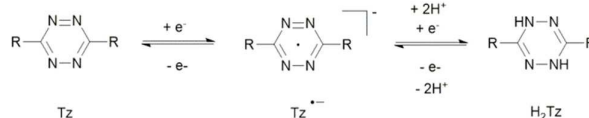
Scheme 1 Reduction of s-Tetrazine (Tz) to Dihydrotetrazine (Tz) via Anion Radical

In our efforts to further explore the photocatalytic activity of pytz and expand its synthetic utility, we report here metal-free efficient oxidation of alcohols to the corresponding carbonyl compounds under visible light irradiation using pytz as catalyst (Scheme 2). During oxidation of alcohols, pytz is converted to H$_2$pytz. In order to reoxidize the H$_2$pytz, an efficient co-oxidant is required. We have utilized O$_2$ or *tert-*

butylnitrite/AcOH mixture as sacrificial co-oxidant to establish two alternative methods of oxidation.
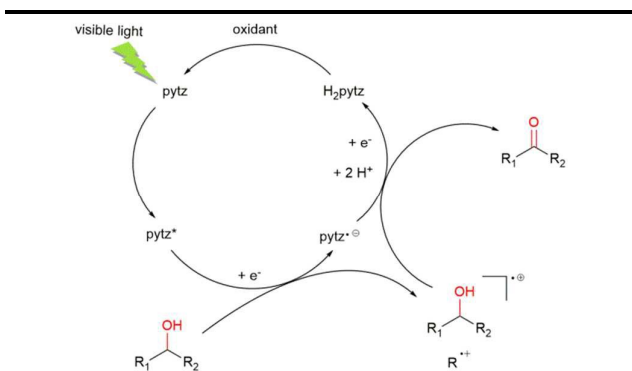
Scheme 2 Oxidation of Alcohols to Carbonyls by Pytz Under Visible Light Irradiation

Results and discussion

Our preliminary studies were carried out with benzyl alcohol **1a** as a model substrate in presence of pytz in CH_3CN. In a typical experiment, benzyl alcohol **1a** in CH_3CN was irradiated under visible light in presence of 5 mol% of pytz catalyst at am-

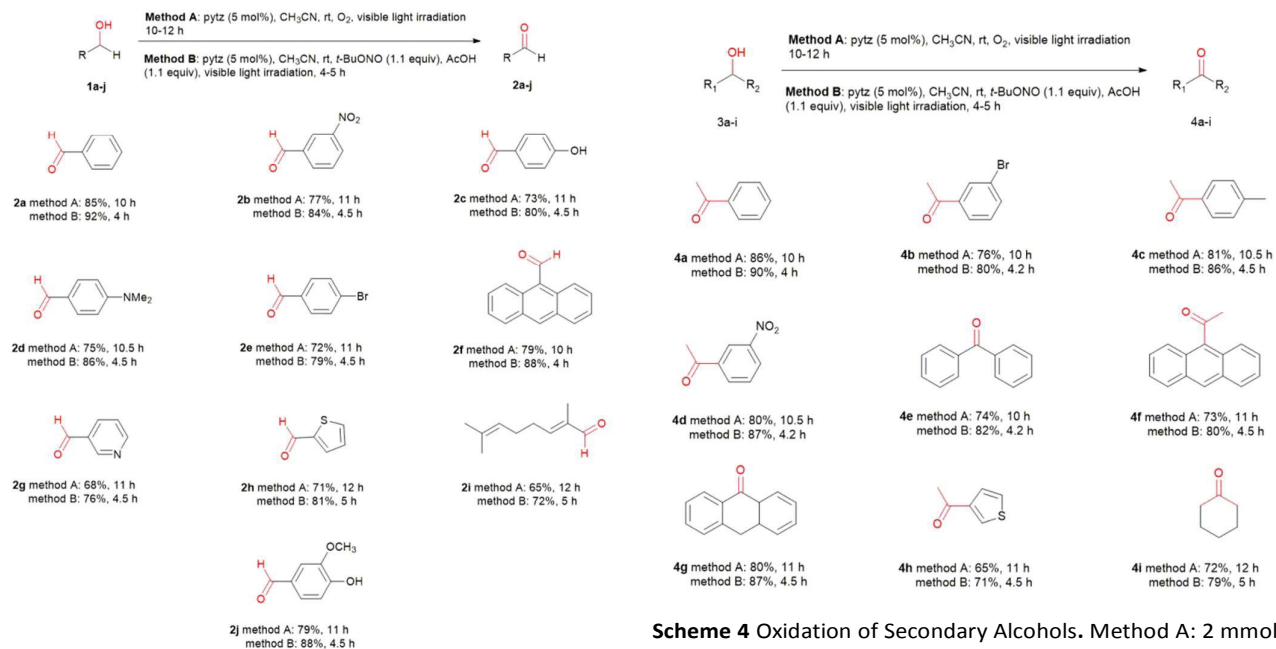**Table 1** Optimization of the Reaction Conditions[a]
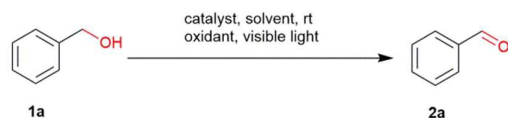
entry	catalyst	solvent	time (h)	yield (%)[b]
1[c]	pytz	CH_3CN	12	traces
2[d]	pytz	CH_3CN	12	13
3	pytz	CH_3CN	10	85
4	pytz	H_2O	12	26
5	pytz	dioxane	12	30
6	pytz	THF	12	42
7	pytz	CH_3Cl	12	55
8	pytz	CH_2Cl_2	12	48
9	pytz	DMF	12	38
10	phtz	CH_3CN	10	35
11[e]	pytz	CH_3CN	12	traces
12[f]	none	CH_3CN	12	none
13[g]	pytz	CH_3CN	4	92
14[g]	none	CH_3CN	5	none

[a]Reaction Condition (until otherwise specified): 2 mmol benzyl alcohol, solvent (5 mL solvents used for all cases), pytz (5 mol%), O_2-atmosphere, room temperature, visible light. [b]Isolated yield. [c]Reaction done in inert atmosphere. [d]Reaction done in presence of air. [e]Reaction carried out in absence of visible-light (dark). [f]Reaction carried out without any catalyst but in presence of visible-light. [g]Reaction carried out in presence of tert-butylnitrite (1.1 equiv), AcOH (1.1 equiv).

bient temperature. Use of 5 mol% of pytz catalyst was found to be optimum and any other substrate to catalyst ratio furnished inferior yields. A Xenon lamp with a power of 300 W equipped with a cut-off filter ($\lambda > 420$ nm) was used as a visible light source (for schematic diagram of reaction set-up, see Scheme S1[†]). Under nitrogen, only trace of the desired product **2a** was obtained (Table 1, entry 1). Changing from oxygen-free environment to aerobic condition resulted in a substantial improvement in conversion (entry 2). Then we have considered the use of pure molecular oxygen. Accordingly, the conversion increased dramatically when reaction was carried out under O_2-atmosphere (entry 3). No noticeable over oxidation to carboxylic acid was isolated or identified. Performing the reaction in other solvents including water, dioxane, THF, chloroform, or dichloromethane gave much lower yields of **2a** (entries 4–9). We have also investigated the catalytic activity of the 3,6-diphenyl-1,2,4,5-tetrazine (phtz), under identical conditions (entry 10). Phtz shows much inferior activity. To establish that visible light is essential for the reaction to proceed, a control reaction was carried out in the dark in presence of pytz. No catalytic activity was observed in the absence of visible light, which clearly demonstrates the role of visible light in this reaction (entry 11). Similarly, a control reaction in the absence of pytz did not proceed under identical conditions (entry 12). Encouraged by these results, we further carried out the reaction in presence of tert-butylnitrite/acetic acid (AcOH) mixture as oxidant. Oxidation of H_2Tz by $NaNO_2$/acid mixture is long known.[22] In the presence of air, these generate nitrogen dioxide, a sufficiently strong oxidant to efficiently recycle the H_2Tz. The effect of reaction time and solvent on the reaction was again evaluated thoroughly. Interestingly, the reaction proceeds within much lower time in CH_3CN (entry 13). No product was obtained when a control reaction was done in presence of tert-butylnitrite/AcOH mixture but without catalyst in presence of visible light (entry 14). So, the optimum reactions were found to involve **1a**, pytz (5 mol%), and O_2 in CH_3CN at ambient temperature under visible light irradiation (Method A, Scheme 3), and **1a**, pytz (5 mol%), tert-butylnitrite (1.1 equiv), and AcOH (1.1 equiv) in CH_3CN at ambient temperature under visible light irradiation (Method B, Scheme S2[†]).

Having the optimum conditions in hands, the scope for the oxidation was subsequently investigated with various primary alcohols; reactions under oxygen environment (method A) are shown for comparison. As shown in Scheme 3, high yields were obtained for a wide range of alcohols. Under these reaction conditions, various benzylic alcohols with different substituents on the phenyl ring containing both electron-withdrawing and electron-donating can be efficiently oxidized to the corresponding aldehydes in high yields (Scheme 3, **2a-e**). Anthracen-9-ylmethanol (**1f**) and heterocyclic alcohols (**1g** and **1h**) were smoothly oxidized to give the aldehydes in good yields (Scheme 3, **2f-h**). In addition, primary allylic alcohol (**1i**) and β-O-4 lignin model, 4-(hydroxymethyl)-2-methoxyphenol (**1j**), were also effective substrates, affording the corresponding aldehydes in good yields (Scheme 3, **2i** and **2j**). The present catalytic system is not efficient for aliphatic prima-

Method A: pytz (5 mol%), CH$_3$CN, rt, O$_2$, visible light irradiation 10-12 h

Method B: pytz (5 mol%), CH$_3$CN, rt, t-BuONO (1.1 equiv), AcOH (1.1 equiv), visible light irradiation, 4-5 h

1a-j → 2a-j

2a method A: 85%, 10 h
method B: 92%, 4 h

2b method A: 77%, 11 h
method B: 84%, 4.5 h

2c method A: 73%, 11 h
method B: 80%, 4.5 h

2d method A: 75%, 10.5 h
method B: 86%, 4.5 h

2e method A: 72%, 11 h
method B: 79%, 4.5 h

2f method A: 79%, 10 h
method B: 88%, 4 h

2g method A: 68%, 11 h
method B: 76%, 4.5 h

2h method A: 71%, 12 h
method B: 81%, 5 h

2i method A: 65%, 12 h
method B: 72%, 5 h

2j method A: 79%, 11 h
method B: 88%, 4.5 h

Scheme 3 Oxidation of Primary Alcohols. Method A: 2 mmol alcohol, acetonitrile (5 mL), pytz (5 mol%), O$_2$-atmosphere, room temperature, visible light; Method B: 2 mmol alcohol, acetonitrile (5 mL), pytz (5 mol%), room temperature, visible light, t-BuNO$_2$ (2.2 mmol), AcOH (2.2 mmol). Isolated yields are shown.

Method A: pytz (5 mol%), CH$_3$CN, rt, O$_2$, visible light irradiation 10-12 h

Method B: pytz (5 mol%), CH$_3$CN, rt, t-BuONO (1.1 equiv), AcOH (1.1 equiv), visible light irradiation, 4-5 h

3a-i → 4a-i

4a method A: 86%, 10 h
method B: 90%, 4 h

4b method A: 76%, 10 h
method B: 80%, 4.2 h

4c method A: 81%, 10.5 h
method B: 86%, 4.5 h

4d method A: 80%, 10.5 h
method B: 87%, 4.2 h

4e method A: 74%, 10 h
method B: 82%, 4.2 h

4f method A: 73%, 11 h
method B: 80%, 4.5 h

4g method A: 80%, 11 h
method B: 87%, 4.5 h

4h method A: 65%, 11 h
method B: 71%, 4.5 h

4i method A: 72%, 12 h
method B: 79%, 5 h

Scheme 4 Oxidation of Secondary Alcohols. Method A: 2 mmol alcohol, acetonitrile (5 mL), pytz (5 mol%), O$_2$-atmosphere, room temperature, visible light; Method B: 2 mmol alcohol, acetonitrile (5 mL), pytz (5 mol%), room temperature, visible light, t-BuONO (2.2 mmol), AcOH (2.2 mmol). Isolated yields are shown.

ry alcohols and shows relatively poor yields (< 40%).

Secondary alcohols were also found to be effective substrates and generally more reactive than primary alcohols. Various secondary aryl alcohols were effectively oxidized to ketones (Scheme 4, entries **4a**-**g**). A number of functionalities, such as bromine, methyl, nitro, and diphenylmethanol are compatible with the reaction conditions and furnished the corresponding ketones in excellent yields (Scheme 4, **4b**-**e**). 1-(Anthracen-9-yl)ethan-1-ol (**3f**) and 9,10-dihydroanthracen-9-ol (**3g**) underwent smooth oxidation to provide the ketones in good yield (Scheme 4, **4f** and **4g**). Furthermore, heterocyclic secondary alcohol, 1-(thiophen-3-yl)ethan-1-ol (**3h**) and alkyl secondary alcohol, cyclohexanol (**3i**), were also effectively oxidised to corresponding ketones (Scheme 4, **4h** and **4i**) with 71 and 79% yields, respectively by method B.

The visible light driven mild pytz-catalysed oxidation of alcohols to carbonyls also proved easy to scale up, as demonstrated by a gram scale experiment in which 20 mmol of benzyl alcohol in 50 mL of acetonitrile (**1a**) was irradiated under visible light in presence of t-BuONO/AcOH. The reaction resulted in 2.06 g (19.4 mmol, 97% yield) of analytically pure benzaldehyde in 7 h.

To understand this visible light driven oxidation of alcohols to carbonyls catalyzed by pytz, a detailed investigation on the mechanism was undertaken. Due to their electron deficient character, tetrazine molecules can be reversibly reduced in organic solvents. Almost all Tetrazine molecules accept one

electron to produce an anion radical which is very stable in absence of any proton donor.[22c,23] Most of the tetrazine derivatives can accept a second electron though this process is not electrochemically reversible in standard conditions. The unstable dianion formed after transfer of second electron reacts with proton donor to give dihydrotetrazine[22c] as shown in Scheme 1. Fukuzumi et al. reported the reduction of 3,6-diphenyl-s-tetrazine (PhTz) by 10-methyl-9,10-dihydroacridine (AcrH$_2$) promoted by scandium ion.[24] In presence of Sc^{3+}, hydride transfer from AcrH$_2$ or 10,10'-dimethyl-9,9'-biacridine [(AcrH)$_2$] to PhTz occurs efficiently at room temperature to yield 10-methylacridinium ion (AcrH$^+$). So, tetrazines can be utilized as two electron oxidising agent under suitable conditions.

In order to elucidate the mechanism of the present direct alcohol oxidation, the optical and electrochemical properties of the pytz molecule were studied by UV–vis absorption spectroscopy and cyclic voltammetry in acetonitrile. Pytz exhibits maximum absorption peaks at 532 nm (ε = 190 M^{-1} cm^{-1}, Fig. 2a) and two quasi-reversible reduction peak at +0.31 and −0.91 V in acetonitrile (Fig. 2b and c). Pytz molecule successively accepts two electrons quasi-reversibly in acetonitrile and can be conveniently converted into H$_2$pytz in presence of proton donor. Occurrence of first reduction potential at +ve potential indicates that pytz molecule is highly susceptible towards reduction and forms stable anion radical.

While a precise understanding of the reaction mechanism awaits further study, a plausible catalytic pathway is proposed
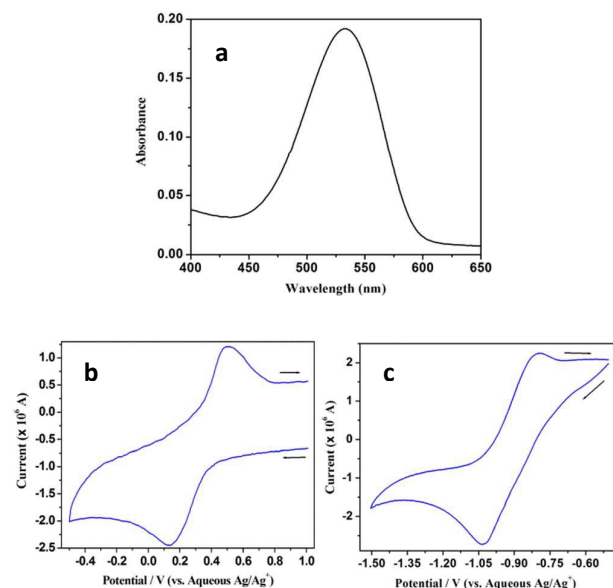
Fig. 2 (a) UV-vis absorption spectra and cyclic voltammogram (CV) of 3,6-di(pyridin-2-yl)-1,2,4,5-tetrazine (pytz) in acetonitrile in the range (b) +1.0 to −0.5 V and (c) −0.5 to −1.0 V. Scan rate for cyclic voltametic measurements were 50 mVs^{-1}.

in Scheme 2. According to the previous studies,[1a,b,21c,d] we pro-posed that the reaction may proceed through the formation of radical cation, ROH$^{·+}$. In presence of visible light, pytz is converted to pytz*, which is transformed in to pytz radical anion through single electron transfer (SET) from alcohol to form radical cation, ROH$^{·+}$. The poor conversion of aliphatic primary alcohols supports the formation of radical cation as aliphatic primary radical cations are not stable. Then, hydrogen atom abstraction by stable pytz radical anion from the radical cation ROH$^{·+}$ followed by deprotonation gives the carbonyl compound and pytz is subsequently converted to H$_2$pytz. Oxidation of H$_2$pytz to regenerate catalyst, pytz, can easily be carried out in presence of molecular oxygen or *tert*-butylnitrite/AcOH mixture. The overall reaction is as follows (eqn 1):

$$RCH_2OH + pytz = RCHO + H_2pytz \qquad (1)$$

To prove the radical pathway, this reaction was also done in the presence of a radical scavenger, TEMPO (TEMPO = 2,2,6,6-tetramethylpiperidinoxyl). Addition of TEMPO in a 1:1 molar proportion (with respect to benzyl alcohol) to the reaction mixture, only trace yield can be identified by GC. To check the possibility of pytz as the sensitizer of O$_2$ and the activated molecular O$_2$ is the real oxidant, we performed the oxidation reaction of benzyl alcohol in the presence of one equivalent of pytz under inert atmosphere and the reaction yield ~ 80% benzaldehyde within 8 h. These results did not support the involvement of activated molecular O$_2$ as the real oxidant. Moreover, molecular oxygen accepts one electron from activated photocatalysts to produce superoxide anion, O$_2^{·-}$.[2] As pytz molecule itself accepts electron in its excited state to act as an oxidising agent, formation of superoxide is not feasible under present reaction protocol. Hence, the involvement of activated molecular O$_2$ as the real oxidant is ruled out.

Conclusion

In summary, we have developed a highly efficient metal free oxidation of alcohols under visible light irradiation using pytz as catalyst and molecular oxygen or *tert*-butylnitrite as co-oxidant. Various primary and secondary alcohols can be efficiently oxidized under mild conditions to the corresponding aldehydes and ketones in high yields. The present procedure shows the following favourable features: (1) the reaction does not require any metal based oxidant; (2) the reaction proceeds under neutral and mild conditions (neither acid nor base required) and thus making it suitable with acid- or base sensitive substrates; (3) the present method is effective for a wide range of substrates bearing various functional groups; (4) the reaction can also be carried out in presence of molecular oxygen further making it environmentally benign procedure; (5) our developed catalytic system should be suitable for large-scale synthesis of carbonyls from alcohols. Further development of other reaction processes with pytz and related tetrazines is currently underway.

Acknowledgements

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<u>**Graphical Abstract**</u>

Metal Free Visible Light Driven Oxidation of Alcohols to Carbonyls Using 3, 6-Di(pyridin-2-yl)-1,2,4,5-tetrazine (pytz) as Catalyst[†]

Suvendu Samanta and Papu Biswas

3, 6-di(pyridin-2-yl)-1,2,4,5-tetrazine (**pytz**)
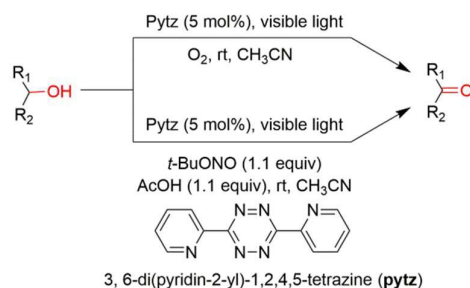
A metal-free photocatalytic system for the transformation of alcohols to corresponding carbonyls in high yields with visible-light irradiation has been achieved. Di(pyridin-2-yl)-1,2,4,5-tetrazine (pytz) was found to be an efficient catalyst for this oxidation under photo irradiation conditions.