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An easy one-step photocatalytic synthesis of 1-aryl-2-alkylbenzimidazoles by platinum loaded TiO₂ nanoparticles under UV and solar light

K. Selvam, M. Swaminathan*

Department of Chemistry, Annamalai University, Annamalainagar 608 002, India

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ABSTRACT

One-pot synthesis of disubstituted benzimidazoles from N-substituted 2-nitroanilines or 1,2-diamines with 3–12 nm-sized platinum particles loaded on the TiO₂ using solar and UV-A light is described. 1-Aryl-2-alkylbenzimidazoles from 2-nitrodiphenylamines are formed by combined redox photocatalytic reaction, condensation and catalytic dehydrogenation on Pt-TiO₂. In case of diamines, this reaction is proceeded by Pt-TiO₂ assisted photocatalytic oxidation of an alcohol and a catalytic dehydrogenation of the intermediate on the surface of platinum nanoparticles. In both cases product formation was achieved by tandem photocatalytic and catalytic reactions on Pt-TiO₂.

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Benzimidazoles play a vital role in the synthesis of pharmaceuticals.¹ 2-Substituted benzimidazoles are used as anthelmintics in veterinary medicine² and display significant anticancer, antiviral, antiallergic, antiulcer, and anticoagulant properties in human therapeutics.³ Methods of benzimidazole synthesis include the condensation of o-aryldiamines and aldehyde in refluxing nitrobenzene,^{4,5} the condensation of *o*-aryldiamines with carboxylic acids or their derivatives in the presence of strong acids such as polyphosphoric acid⁶ or mineral acids⁷ and the thermal or acid promoted cyclization of *N*-(*N*-arylbenzimidoyl)-1,4-benzoquinoneimines.⁸ Direct condensation of o-aryldiamines and aldehydes is not a good synthetic reaction, as it is well known to yield a complex mixture of 1,2-disubstituted benzimidazoles, the bis anil and dihydrobenzimidazoles.⁹ However, in this reaction, the addition of a transition metal, namely copper(II) acetate,10 mercury oxide11 or lead tetracetate¹² allows a partial selective synthesis of benzimidazoles. Unfortunately, many of these processes suffer some limitations, such as drastic reaction conditions, low yields, tedious work-up procedures and co-occurrence of several side reactions. This way, the development of clean, general, and selective routes to benzimidazoles, including the use of new catalysts, renewable starting materials, and non-classical energy sources continues to attract the interest of synthetic organic chemists.

In the context of developing eco-friendly green chemical process, we decided to look at the use of photocatalysts for the synthesis of 1-aryl-2-alkylbenzimidazoles. Photocatalysts such as TiO_2 , Pt- TiO_2 and others have been reported for the synthesis of benzimidazoles.^{13–15} Pt- TiO_2 is able to promote two different transformations in one-pot by employing both photocatalytic and catalytic actions: the conversion of nitro to amino group and alcohols into aldehydes through a platinum-assisted photocatalytic redox reaction on the Pt- TiO_2 surface,¹⁵ and the catalytic dehydrogenation of benzimidazoline intermediates generated by the condensation of *ortho*-arylenediamines and aldehydes on the platinum particle surface.

Some of the modified semiconductor photocatalysts developed in our laboratory have been used for several organic transformations.^{16–18} Recently we reported the synthesis of 2-alkylbenzimidazoles by combined redox reaction of 2-nitrophenyl azides in alcohols using Pt-TiO₂ catalyst.¹⁹ In the present study, we report a new strategy for the acid- and oxidant-free synthesis of 1-aryl-2-alkylbenzimidazoles using 2-nitrodiphenylamines or 2-aminodiphenylamines and alcohols at room temperature under UV and solar light. To the best our knowledge this is the first report on the semiconductor mediated one-pot photocatalytic synthesis of 1-aryl-2-alkylbenzimidazoles with good yield under mild conditions. The reaction mechanism and steps taken to validate the mechanism are discussed.

Pt-TiO₂, prepared by photodeposition method,²⁰ was characterized by X-ray diffraction (XRD), high resolution transmission electron microscopy (HR-TEM), X-ray photoelectron spectroscopy (XPS), BET surface area and diffuse reflectance spectroscopy (DRS) techniques (see Supplementary data, Figs. S1–S4). The X-ray diffraction patterns of the Pt-TiO₂ [Fig. S1(b)] samples match





^{*} Corresponding author. Tel.: +91 4144 225072, mobile: +91 9842381967; fax: +914144 238145.

E-mail address: chemres50@gmail.com (M. Swaminathan).

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that of the undoped TiO₂ and are identical with the JCPDS pattern of anatase. This reveals that photodeposition of the platinum does not modify the basic crystal structure of the TiO₂ used. The highresolution transmission electron microscopy (HR-TEM) image of Pt (1.5%)-TiO₂ (Fig. S2) shows non-spherical platinum particles with an average diameter of 3–12 nm. The electronic state of Pt in the catalysts was verified by XPS. The XPS survey spectrum (see Supplementary data, Fig. S3) of the Pt-TiO₂ indicates the peaks of elements Ti, O, C and Pt (trace). High-resolution XPS spectrum (inset Fig. S3) from 80 to 90 eV confirms the existence of Pt. Figure S3 shows the binding energies of Pt4f_{7/2} (70.3 eV) and Pt4f_{5/2} (74.0 eV) and the splitting of the 4f doublet (3.7 eV). These binding energies indicate that platinum is present in metallic state. The diffuse reflectance spectrum of 1.5% Pt-doped TiO₂ is shown in Figure S4. Pt-TiO₂ has higher absorption in the visible region.

Initial experiments were carried out with ethanolic solution of 2-nitrodiphenvlamine (1) containing TiO_2 nanoparticles under different conditions. Irradiation of 2-nitrodiphenylamine with TiO₂ in ethanol using UV light produced cyclized product of 2-methyl-1phenylbenzimidazole (2).²¹ Either the irradiation of ethanolic solution of 2-nitrodiphenylamine alone or the solution of 2-nitrodiphenylamine and the catalyst without light did not give any product of our interest. This indicates that both light and TiO₂ are essential for the formation of 2-methyl-1-phenylbenzimidazole. With pure TiO₂ (Table 1, entry 1), 8 h photoirradiation was required to obtain 75% of product 2 in addition to small amounts of other reduction products (12%). The structure of product 2 was confirmed by GC-MS and NMR.²² The percentage yield was determined by comparison with the retention times of authentic samples and by co-injection with the authentic compounds. The main product identified was 2-methyl-1-phenylbenzimidazole. In contrast, Pt (1.5%)-TiO₂ promoted the rapid and selective production by achieving 92% yield of product 2 with 4 h irradiation (Table 1, entry 4). Higher yield (92%) by Pt-TiO₂ with half the time required for TiO₂ reveals the efficiency and selectivity of Pt-TiO₂ in this reaction. Best results were obtained with 50 mg of the catalvst. Lower loading resulted in lower yields, while higher loading did not increase product vields significantly. The percentage vields of the product with 0.5 and 1 wt % of platinum content are 72.0 and 83.0%, respectively (Table 1, entries 2 and 3). The same reaction when performed without catalyst for 4 h gave no product. When the platinum content was increased to 2 wt %, the product yield decreased to 87.0% (Table 1, entry 5). Hence 1.5 wt % of platinum

Table 1

Comparison of catalytic efficiencies for the photocatalytic synthesis of 2-methyl-1phenylbenzimidazole from 2-nitrodiphenylamine

Entry	Catalyst	Time (h)	Products yield (%)	By product (%)	Conversion ^a (%)
1	Prepared TiO ₂	8	2-Methyl-1- phenylbenzimidazole (75)	12	87.0
2	Pt (0.5%) TiO ₂	4	2-Methyl-1- phenylbenzimidazole (72)	8	80.0
3	Pt (1.0%) TiO ₂	4	2-Methyl-1- phenylbenzimidazole (83)	5	88.0
4	Pt (1.5%) TiO ₂	4	2-Methyl-1- phenylbenzimidazole (92)	4	96.0
5	Pt (2.0%) TiO ₂	4	2-Methyl-1- phenylbenzimidazole (87)	5	92.0

All reactions were performed with a 25 mM ethanolic a reactant 50 mg of catalyst suspension, $I = 1.381 \times 10^{-6}$ einstein L⁻¹ s⁻¹.

^a Remaining nitroaniline.

was found to be the optimum level. Encouraged by this initial result, we set out to examine the scope and limitations of this procedure.

Having completed this optimization study, we proceeded to investigate the reaction with different alcohols using 2-nitrodiphenylamine (Table 2). Moderate to good yields (40-96%) of 2-substituted phenylbenzimidazoles were obtained from methanol, ethanol, propanol and butanol (entries 1-4) under the same conditions. Except in isopropanol, corresponding benzimidazoles were formed in other alcohols. The yield of benzimidazole in ethanol was high (96%), whereas the yield of benzimidazole in methanol was low (40%). The yield decreased from ethanol to butanol (96 to 75%) gradually. Spectral and GC–MS data of the products formed from methanol, ethanol, propanol and butanol are given in Ref.²² In case of isopropanol, acetone is formed and it is less likely to undergo condensation with 1.2-diamine due to steric effect.¹³ Hence only the reduction of nitro group to amine was observed. This reaction was very slow with aromatic alcohols such as benzyl alcohol and the product formed was less than 5% even for 8 h irradiation.

With the same reaction conditions, we screened a series of *N*-aryInitroanilines and *N*-alkyInitroanilines with alcohols, which resulted in the formation of either *N*-aryIbenzimidazoles or *N*-alkyIbenzimidazoles (Table 3). Both 1-aryI- and 1- alkyI -substituted benzimidazoles were successfully produced in very good yields. These reactions were carried out with this catalyst under direct solar light and the results are compared with UV process. The trend observed in solar light is similar to the one in UV light (Table 3), but the efficiency is found to be more in UV light than in solar light.

Semiconductor oxide provides a microheterogeneous center for oxidation and reduction and so simultaneous oxidation of alcohol to aldehyde and reduction of nitro to amine group take place. This is followed by the condensation of amine and aldehyde leading to a cyclized product. A mechanism for the formation of 2-methyl-1phenylbenzimidazole from 2-nitrodiphenylamine in ethanol is proposed in Scheme 1. TiO₂ on irradiation produces electron and hole (h⁺) pair. The h⁺ oxidizes ethanol to acetaldehyde while the electron reduces the nitro compound **1** to amino compound **2** on the surface. Oxidation of alcohol and reduction of nitro group by semiconductor photocatalyst has been well established.¹³ Compound **2** undergoes spontaneous condensation with aldehyde producing a mono imine intermediate **3**. Cyclization of this intermediate gives 2-methyl-*N*-phenylbenzimidazoline **4**, which on

Table 2

Results obtained on 4h irradiation (365 nm) of 2-nitrodiphenylamine with 1.5% wt Pt-TiO_2 nanoparticles in different alcohols

Entry	Alcohols	Products yield (%)	By product (%)	Conversion ^a (%)
1	2- Nitrodiphenylamine/ ethanol	2-Methyl-1- phenylbenzimidazole (92)	4	96
2	2- Nitrodiphenylamine/ propanol	2-Ethyl-1- phenylbenzimidazole (90)	9	99
3	2- Nitrodiphenylamine/ butanol	2-Propyl-1- phenylbenzimidazole (75)	5	80
4	2- Nitrodiphenylamine/ methanol	1- Phenylbenzimidazole (40)	6	46
5	2- Nitrodiphenylamine/ isopropanol	2- Aminodiphenylamine (95)	4	99

All reactions were performed with a 25 mM alcoholic solution of a reactant 50 mg of catalyst suspension, $I = 1.381 \times 10^{-6}$ einstein L⁻¹ s⁻¹.

^a Remaining nitroaniline.

 Table 3

 Results obtained on irradiation (365 nm) of various N-substituted 2-nitroanilines with Pt-TiO2 nanoparticles in different alcohols

Entry	Nitroaniline	Alcohol	Product	UV	Solar
1	H H H H H H H H H H	ОН	N N CH ₃	92	82
2	H NO ₂	ОН	N N C ₂ H ₅	90	80
3	H NO ₂	ОН	N N C ₃ H ₇	75	71
4		ОН		90	70
5		ОН		80	63
6		ОН		72	60
7	HN CH ₃	ОН	N N CH ₃	96	91
8	HN ^{CH₃} NO ₂	ОН	$\mathbb{V}_{C_{2}H_{5}}^{N}$	95	84
9	HN ^{CH} ₃ NO ₂	ОН	$ \begin{array}{c} $	90	79
10		ОН	$\bigcup_{\substack{N\\ C_2H_5}}^{N} CH_3$	92	90
11		ОН	$ \begin{array}{c} \overbrace{}^{N} \\ \underset{}{\overset{N}{\overset{N}{\overset{C}}}} \\ \underset{}{\overset{N}{\overset{C}{\overset{N}{\overset{N}}}} \\ \end{array} $	88	83
12	NO ₂	ОН	$\underset{\substack{I \\ C_2}}{\overset{N}{}} C_3H_7$	82	77
13		ОН	CI N CH ₃	86	86

Iddle 5 (continued	Table 3	(continued
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Entry	Nitroaniline	Alcohol	Product	UV	Solar
14		ОН	CI N C ₂ H ₅	80	71
15		ОН		70	63
16		∕он		95	87
17	NO ₂ H NC ₂ H Cl	ОН		78	72
18	NO _{2 H} N CI	ОН	N N C ₃ H ₇	70	61

oxidation forms 2-methyl-*N*-phenylbenzimidazole **5**. The higher conversion of 2-nitrodiphenylamine with 1.5% Pt-TiO₂ (Table 1, entry 4) is due to the trapping of electrons by Pt on the excited TiO₂. The electrons excited from the valence band of TiO₂ to the conduction band are efficiently transferred to Pt due to the charge separation effect and accumulated therein. The oxidant (alcohol) and the reductant (*N*-substituted 2-nitroanilines) are abundantly supplied to the oxidation (TiO₂), and reduction sites (Pt), respectively by a reasonable delivery effect facilitating a combined redox reaction. Further platinum, present in Pt-TiO₂, catalyzes the oxidation of benzimidazoline. This catalytic dehydrogenation was reported earlier by Shiraishi et al.¹⁵

As the catalyst was used earlier for benzimidazole synthesis from *o*-phenylenediamines,¹⁵ we extended the use of this catalyst with N-substituted 1,2-diamines. Thus, N-substituted diamines with alcohols gave the corresponding benzimidazoles in good yield under both UV and solar light (Table 4). Thermal synthesis of benzimidazoles from N-substituted diamines was reported to be unsuccessful.²³ Therefore this methodology is ideal for preparing 1-alkylated-2-substituted benzimidazoles from N-substituted diamines. In case of benzyl alcohol and 4-chlorobenzyl alcohol, the reaction was slow and the yield was less (Table 4, entries 19 and 20) when compared to other alcohols. When N-hydroxyethyl-1,2-diamine was used with ethanol, propanol and butanol, the products formed were similar to the products formed with 1,2-diamine (Table 4, entries 13, 14 and 15). This shows that the hydroxyl ethyl group is eliminated before cyclization due to steric effect. Since the benzimidazole formation starts from substituted 1,2-diamines, same mechanism proposed in Scheme 1 is followed in this reaction also.

In conclusion, $Pt-TiO_2$ enables efficient benzimidazole production under photoirradiation conditions. This is promoted by one-pot multiple catalytic transformations on $Pt-TiO_2$, which involve a platinum-assisted photocatalytic oxidation on TiO_2 and a



Scheme 1. Photocatalytic and catalytic pathway of Pt-TiO₂ on synthesis of *N*-substituted benzimidazoles.

catalytic dehydrogenation on the surface of the platinum particles. This process has significant advantages when compared with other methods: (i) a cheap and stable reactant (alcohol), (ii) it does not require the use of acids or oxidants and (iii) the reaction proceeds

Table 4

Results obtained on irradiation (365 nm) of various N-substituted 1,2-diamines with Pt-TiO₂ nanoparticles in different alcohols

Entry	Diamine	Alcohol	Product	UV	Solar
1	H H2	ОН	N N CH ₃	98	85
2	H NH ₂	ОН	N N C ₂ H ₅	90	83
3	H NH ₂	ОН	N N C ₃ H ₇	75	77
4		ОН	CI N-CH ₃	95	86
5		ОН		82	74
6		ОН	CI N C ₃ H ₇	76	69
7	HN ^{CH3} NH ₂	ОН	N N CH ₃	97	87
8	HN ^{CH} 3 NH ₂	ОН	$ \begin{array}{c} & & \\ & & $	87	79
9	HN ^{CH3} NH2	ОН	$\underset{CH_{3}}{\overset{N}{\underset{CH_{3}}{\overset{L}{\underset{CH_{3}}{\overset{L}{\underset{C}{\overset{L}{\underset{C}{\underset{C}{\overset{L}{\underset{C}{{\atopC}}{\underset{C}{\underset{C}{\atop{C}}{\underset{C}{\atop{C}}{\underset{C}{{\atopC}}{\atop{C}{\atopC}}{\atop{C}}{\atop{C}}{{C}}}}}}}}$	81	71
10		ОН	$\underset{C_2H_5}{\overset{N}{\longrightarrow}}CH_3$	92	88
11		ОН	$ \begin{array}{c} $	86	73
12	N, CH ₃ NH ₂	ОН	$ \begin{array}{c} \searrow \\ N \\ N \\ C_{2}H_{5} \end{array} $	80	75
13		ОН	CI N CH ₃	92	88

Entry	Diamine	Alcohol	Product	UV	Solar
14		ОН	CI N C ₂ H ₅	86	73
15		ОН		80	75
16	NH ₂ H N Cl	ОН		85	81
17	NH ₂ H CI	ОН		72	64
18	NH ₂ H CI	ОН		60	62
19	H NH ₂	ОН		40	31
20	H NH ₂	СІ		35	27

Table 4 (continued)

under mild ambient conditions. Therefore, this process has the potential for a sustainable synthesis of 1-aryl-2-alkylbenzimidazole from N-substituted nitroanilines and 1,2-diamines.

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Supplementary data

Supplementary data (synthesized compounds and characterization of $Pt-TiO_2$ by X-ray diffraction (XRD), High resolution transmission electron microscope (HR-TEM), and diffuse reflectance spectroscopy (DRS)) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.04.090.

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- 20. Pt(x)-TiO₂ samples, containing different platinum loadings [x (wt %) = Pt/(TiO₂ + Pt)100; x = 0.5, 1.0, 1.5, 2.0] were prepared by a conventional

photodeposition method, in which photoirradiation of an aqueous solution home made TiO_2 with hexachloroplatinic acid (HPtCl₄·4H₂O) afforded gray powder of the Pt-TiO₂ catalyst.

21. The photocatalytic and catalytic synthesis was carried out using the following procedure. Appropriate amounts of catalyst and 2-nitrodiphenylamine or 2aminodiphenylamine in 25 mL of alcohol were taken in a reaction tube. The reaction tube was sealed with a rubber septum and purged with nitrogen for 30 min. The reaction mixture was irradiated with UV (365 nm) mediumpressure mercury lamp (Sankyo Denki, Japan; intensity $l = 1.381 \times 10^{-6}$ einstein $L^{-1} s^{-1}$)/ solar light at constant stirring. The temperature of the reaction medium during UV irradiation was 32 °C and it was nearly constant. With solar light, the temperature of the solution changed gradually from 32 to 48 °C for all the experiments. The progress of the reaction was monitored using thin layer chromatography (TLC). Product analysis was performed by GC analysis, Perkin-Elmer GC-9000 with a capillary column of DB-5 and flame ionization detector was used. GC-MS analysis was carried out using Varian 2000 Thermo with the following features: capillary column VF5MS (5% phenyl-95% methylpolysiloxane), 30 m length, 0.25 mm internal diameter, $0.25\,\mu m$ film thickness, temperature of column range from 50-280 °C (10 °C/min) and injector temperature 250 °C, attached with mass spectrometer model SSQ 7000. The isolation was performed by column chromatography on a silica gel column by eluting with a co-solvent of dichloromethane and methanol (volume ratio: 8:2). For solar experiments, all reactions have been carried out under similar conditions on sunny days of different months of 2008–2009 between 10 A.M. and 2 P.M. The intensity of solar light was measured using a LT Lutron LX–10/A digital Lux meter and it was found to be 1250×100 (±100) lux. The intensity was nearly constant during the experiments.

- 2. 2-methyl-1-phenyl benzimidazole: ¹H NMR: 2.46, s, 3H, CH₃, 7.06–7.75, m, 9H, Ar-H's. ¹³C NMR: 12.21 CH₃, 135.99, 136.42, 142.57, 151.53, ipso C's, 109.98–129.95, Ar-C's. GC-MS (m/z): 208 (M^{*})166, 152, 130, 76, 63, 51, 39.
 2-ethyl-1-phenyl benzimidazole: ¹H NMR: 1.33, t, 3H, CH₃, 2.77, q, 2H, CH₂, 7.08–7.78, m, 9H, Ar-H's. ¹³C NMR: 14.6 CH₃, 21.33 CH₂, 136.08, 136.67, 142.59, 156.36, ipso C's, 110.00–130.00, Ar-C's. GC-MS (m/z): 222 (M+)166, 152,130,76,63,51,39. IR (KBr) (cm⁻¹) = 1613, 1596, 1520, 1499, 1455, 1398, 1275, 1228, 1189, 1070, 1020, 743, 704 cm⁻¹.
 1-phenyl-2-propyl benzimidazole: ¹H NMR: 0.86, t, 3H, CH₃, 2.69, t, 2H, CH₂ CH₃, 1.75, m, 2H, CH₂CH₂ CH₃, 6.99–7.74, m, 9H, Ar-H's. ¹³C NMR: 13.98 CH₃, 21.25 CH₂CH₂CH₃, 29.65 CH₂CH₂CH₃, 136.01, 136.56, 142.61, 155.17 ipso C's, 110.01–129.96 Ar-C's. GC-MS (m/z): 236 (M+).
 1-phenyl benzimidazole: ¹H NMR: 8.2,s, 1H, 7.93–7.78,m, 1H, 7.77–7.50,m, 6H, 7.45–7.35,m, 2H; ¹³C NMR: 14.40, 142.3, 136.4, 133.7, 128.1, 124.1, 123.7, 122.8, 120.6, 110.5; GC-MS (m/z): 195.0 [M+H]*.
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