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Hydroxyl Radical Mediated an Improved Photocatalytic Baeyer–Villiger Oxidation to Synthesize L-Dopa Derivative from L-Tyrosine

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ABSTRACT

The arena of visible light-mediated photochemistry has experienced significant progress, leading to the development of a wide array of methodologies in synthetic organic chemistry. In particular, photocatalysis by using long-wavelength light, such as red/green or blue, has attracted significant attention. In this regard, the Baeyer–Villiger (B–V) oxidation of ketones to the corresponding lactones/esters is one of the definitive and crucial reactions in the chemical industry. However, this oxidation process has not yet been studied in ambient conditions with the aid of hydroxyl radicals using purely organic photocatalysts, especially on the synthesis of amino acids like L-dope. For a long time, L-dopa and its derivatives were synthesized and investigated for their enormous pharmacological activities and their capabilities to be converted into other natural and unnatural products, which have a great biological interest. Herein, transition metal-free organic dyes have been utilized as photocatalysts for the assistance of B-V-rearrangement, which has been developed in the final step to produce a much improved yield of L-dopa derivative with minimal byproducts, under mild conditions and without any racemization of the chiral center.

Keywords: Photocatalysis, Baeyer–Villiger oxidation, L-dopa, Parkinson's disease, Anticancer.

I. INTRODUCTION

In the middle of the 20th century, L-3,4-Dihydroxyphenylalanine (L-DOPA) was just known as an intermediate in the biological synthesis of Epinefrine[1] and Malanine[2]. Over the past few decades, L-DOPA (**1**) (Fig.1) has been established as an excellent natural remedy for neurological disorders[3] like Parkinson's disease.[4] The administration of L-DOPA was the way to reestablish cerebral concentration of dopamine, which made great advances in the treatment of the disease[5] and increased demand for this optically pure substance. L-DOPA is also a precursor of other very important neurotransmitters like norepinephrine (noradrenaline) and epinephrine (adriline), which are also released by the brain and central nervous system (CNS) Activity of L-Tyrosine in the human body or in microorganisms is very weak in general. Both L-Tyrosine and L-DOPA are rapidly decomposed into other metabolites. Hence, design and synthesis and extended biological evaluation of L-DOPA derivatives in vivo as well as in vitro could be a potential prodrug for not only the treatment of Parkinson's disease but also others

variety of diseases. Even some derivatives of L-dopa were found to be more active[6] than L-DOPA (**1**) itself, so they could be used as prodrugs. In addition to that, L-dopa derivatives are also used to synthesize several natural products[7] such as Isodityrosine (**2**) is a naturally occurring dimeric amino acid that is a key structural unit of a large group of biologically active compounds, e.g., piperazinomycin (**3,** Fig.1), O.F-4949s, K-13, etc., which have confirmed immune potentiating and antitumor properties. Hence, these generate great biological importance to treat a range of diseases, even the treatment of deadly cancer.

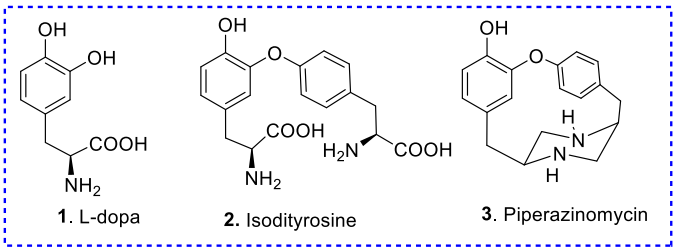


Figure-1. L-dopa and some L-dopa-containing natural products.

The idea of using visible light to promote organic reactions is not very new; rather, it is more than a century old. Giacomo Ciamician, an Italian chemist, and his colleague, Paul Silber, first performed photochemical reactions using visible light.[8] Unfortunately, despite all the fascination, the domain was still not considered friendly, mostly due to the production of lots of byproducts by the employment of shorter wavelengths falling in the UV and far visible range, and tedious reaction conditions. In 2008, the MacMillan group changed the perception using visible light induced photoredox catalysis, which enabled to efficiently perform photochemical organic transformation, making a milestone leap in organic synthesis and catalysis.[9] The technological advancement using LEDs as a visible light source, which ensure that precise wavelength matching with the energetics of the organic synthesis can be applied. Problem arises in there as most of them are unable to absorb visible light themselves and rely mostly on transition metal-based photocatalyst[10] or metal-free organic dyes as photocatalyst[11] to get activated through either single electron transfer (SET) or by energy transfers (EnTs). However, despite having excellent photocatalytic properties and yield, metal complexes are very expensive and toxic. Hence, any chemical reaction based on them is likely not sustainable. In recent years, employing organic dyes as metal-free alternatives and sustainable approaches has been achieved for organic synthesis. These organic dyes report significant advantages in comparison to their metal counterparts due to their inexpensiveness, environmental friendliness, non-toxicity, and synthetic versatility. A diverse range of organic dyes, such as Rhodamine B, Eosin Y, Eosin B, methylene blue, and Rose Bengal were explored in organic synthesis (Fig. 2). Compared to other dyes, the utilization of Rose Bengal (RB) as a photocatalyst has received considerable attention as photocatalyst due to its redox potential falls in range with the redox potential of several organic molecules helping in photoinduced electron transfer. After absorption of light, RB is activated to its excited singlet state (RB*) with $t_{1/2}$ ranging from 10^{-6} to 10^{-9} s. The singlet excited state either decays back to the ground state or gets converted to a longer-lived triplet excited state ($t_{1/2}$ = 10^{-3} s) via intersystem crossing (ISC).[12]

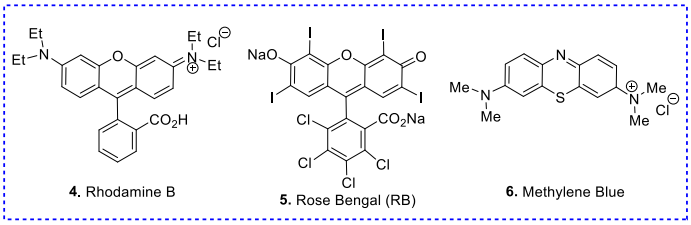


Figure-2. Various organic dyes as photocatalysts.

Conventional synthesis of optically pure L-DOPA was presented by Washer and Lewandowski,[13,] which was based on "chiral pool". After that, many methods have been developed[14] for the preparation of L-DOPA using either chiral pool materials or chiral catalysts. More recently, Chiral phase transfer agent,[15] an ammonium quaternary salt with a C_2 symmetry has been

introduced. However, all these processes are low-yielding, time-consuming, and various hazardous chemical byproducts are formed. Therefore, an urgent need for a suitable, cheap, nature-friendly process to produce optically pure chiral amino acids for the purpose of their intensive use as active pharmaceutical intermediates in the drug industry. Under this purview, I was inspired to undertake the challenge to develop an efficient protocol for this specific synthesis of L-dopa as a part of our ongoing research endeavours.

Because of the technological advantages of photochemical reaction in recent years, photo-catalyzed induced Baeyer–Villiger (B–V) oxidation of ketones to the corresponding lactones/esters[16] has attracted synthetic communities for their much better yield in low temperature, mild reaction conditions, time economy, and atom economy also. However, visible light-assisted synthesis of L-DOPA using metal-free photocatalyst has so far been restricted. In the present work, I tried to develop a simple trick of synthesis of L-Dopa derivative from L-Tyrosine using visible light irradiation as energy source and Rose Bengal (RB) as photocatalyst, and using an appropriate solvent to improve the yield in the final step of Baeyer–Villiger (B–V) oxidation. In this manner, the very old Boger's procedure[17] has been improvised by irradiating simple two Blue LED bulb (Fig. 3). Accordingly, I herein report a visible light-induced green and efficient protocol to access L-dopa derivative from L-tyrosine.

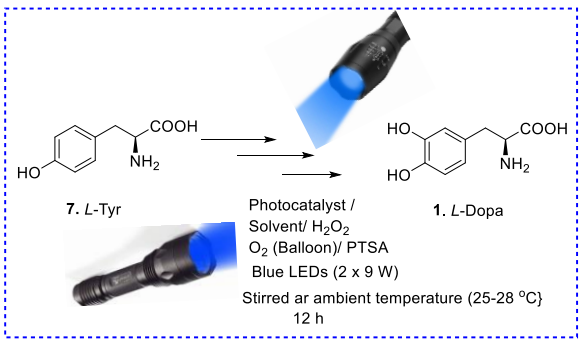


Figure-3. Visible light induced synthesis of L-dopa.

In this photoactivation, O_2 as well as H_2O_2 produce various reactive oxygen species, such as $^*O_2^-$, $^1O_2$, hydroxyl radical (*OH), *OOH, PhCO* and PhCOOO*, which are crucial for driving the B-V-oxidation process. The precise control over reactive species has emerged as a critical tactic in the realm of photocatalytic oxidation.

II. METHODS AND MATERIAL

Preparation of (S)-Methyl3-(4-(benzyloxy)-3-hydrox phenyl)-2-(benzyloxycarbonylamino) Propanoate (**12**):

A solution of Ketone **11** (1gm, 2.15 mmol), 30% H_2O_2 (0.7 ml, 7.1 mmol), p-Toluenesulphonic acid, monohydrate (123 mg, 0.64 mmol, 30 mol%), benzaldehyde (455 mg, 4.3 mmol), and MeCN (2 ml) was taken in an oven-dried tripod standard-joint glass-vessel with a magnetic stir bar in a sequential manner. Oxygen (O_2) was bubbled through the reaction mixture for about 10 s, and the reaction vessel was then capped with a stopper having a vertical channel fitted with an O_2 balloon. This reaction system was now placed (at a distance of 2 cm from the light source) under the influence of blue LEDs (2 × 12 W, 440 nm) within a specially designed wooden box. After that, the reaction mixture was started to stir at room temperature for the stipulated time frame (10–12 h) with occasional TLC monitoring to judge the progress of the reaction. On completion of the reaction, the resulting mixture was then diluted with half-saturated $NaHCO_3$ (5 ml) before being extracted with ethyl acetate (2 × 20 ml) after being shaken well in a separating funnel. The combined organic extracts were washed with water (1 x 20 ml) brine (1 × 20 ml), and then dried over Na_2SO_4. The combined organic solvent was then removed under reduced pressure to obtain a crude mass, which was finally purified through column chromatography

using mixtures of EtOAc–hexane (2: 8 v/v) as eluents, to furnish the desired alcohol **12** as a colourless oil.

Yield: 830mg (89%).

[α]D: - 14.9 (*c* = 1.1, MeOH). [Lit [17][α]D for **ent-8:** - 15.15 (*c* = 1.0, MeOH).

IR (KBr): 3409, 3064, 3033, 2953, 2924, 2852, 1738, 1721, 1610, 1499, 1454, 1379, 1352, 1288, 1245, 1214, 1178, 1138, 1978, 1062, 1026, 812, 797, 773, 738, 697 cm^{-1}.

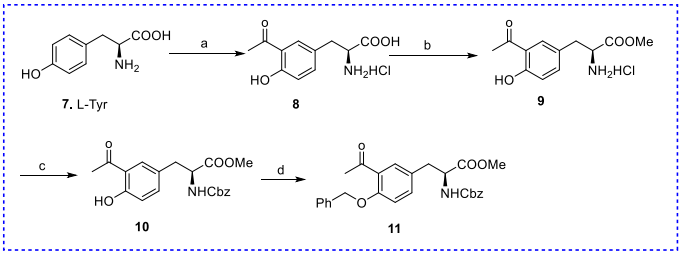
^1H **NMR** ($CDCl_3$, 500 MHz): δ 7.42-7.38 (5 H, m, Ph), 7.37-7.29 (5 H, m, Ph), 6.81 (1 H, d, *J* = 8.2 Hz, C_5-ArH), 6.99 (1 H, d, *J* = 2 Hz, C_2-ArH), 6.55 (1 H, dd, *J* = 8.2, 2 Hz, C_6-ArH), 5.61 (1 H, br s, OH), 5.20 (1 H, d, *J* = 8 Hz, NH), 5.09 (2 H, s, $PhCH_2OAr$), 5.06 (2 H, s, $PhCH_2O_2C$), 4.61 (1 H, q, *J* = 8 Hz, CH_2CHNH), 3.73(3 H, s, OCH_3), 3.04 and 2.90(1H each, two dd, *J* = 16, 8 Hz, CHHCHNH and CHHCHNH).

^{13}C **NMR** ($CDCl_3$, 75 MHz): δ 171.5, 156.2, 145.9, 145.0, 136.3, 135.9, 129.5, 128.7, 128.4, 128.3, 128.1, 128.0, 127.8, 120.9, 115.7, 112.4, 71.1, 67.2, 54.8, 52.7, 37.6.

HRMS (TOF MS ES^+): *m/z* 458. 1583 (M + Na) ($C_{25}H_{25}NaNO_6$); Calcd 458.1580

III.RESULTS AND DISCUSSION

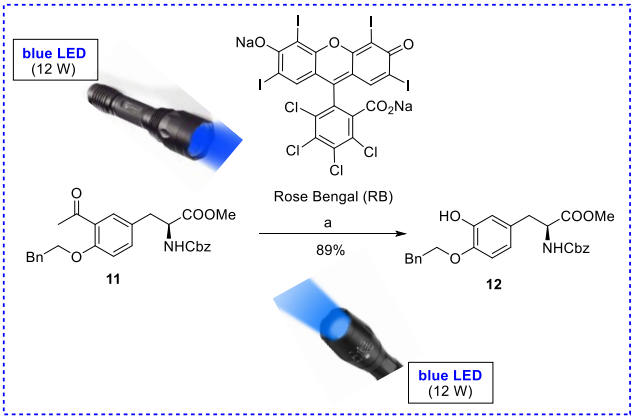
At the beginning of the preparation of the prime precursor of the B-V oxidation process, L-Tyrosine **7** was easily converted to the acylated compound **8** by century-old conventional Friedel-Crafts acylation reaction using acetyl chloride, anhydrous $AlCl_3$ in dry nitrobenzene in very good yield (78%). Esterification of the acid functionality in the latter with CH_3COCl in dry MeOH at rt delivered **9** in excellent yield (91%). Subsequent protection of free amine in **9** with Cbz-group using benzylchloroformate, sodium carbonate in diethyl ether-water, afforded **10** also in high yield (90%). Protection of free phenol in **10** as its benzyl ether using benzyl bromide, K_2CO_3, and tetra-n-butyl-ammonium iodide as catalyst in DMF furnished **11** in quantitative yield again (Scheme-1). All compounds, including **11,** were characterized by IR, rotation, NMR, and mass spectrum, which is quite satisfactory with the literature value.



Scheme 1: Reagents and conditions*:* (a) $AlCl_3$, CH_3COCl, $PhNO_2$, 100 °C, 6 h, 76%; (b) CH_3COCl, MeOH, rt, 2 h, 98%; (c) Benzylchloroformate, Na_2CO_3, Et_2O-H_2O (1:1), rt, 3 h, 90%; (d) benzyl bromide, K_2CO_3, tetra-n-butyl ammonium iodide (cat), DMF, rt, 6 h, 94%.

In previous work, the compound **11** was converted to L-dopa derivative **12** after reduction with sodium borohydride in methanol by an acid-catalyzed benzylic-peroxide rearrangement[17] in the presence of H_2O_2 (30%) and catalytic *p*-TsOH.H_2O in THF in a moderate yield of (61%) by long time heating of the reaction mixture with significant recovery of starting material.

organic photocatalytic irradiated mild Baeyer–Villiger (B–V) reaction of L-Dopa derivative had hardly been tried to the best of my knowledge due to its complicated structure and many functionalities around the benzene ring. Therefore, with the key precursor **11** in hand**,** I next focused on improving the yield of **12** by visible light-assisted conditions using a shoutable organo photocatalyst.



Scheme-2: (a) Rose Bengal (Cat, 1 mol%), 30% aq. H_2O_2, p-Tolune sulphonic acid (PTSA) (10 mol %), Benzaldehyde (2 eqv.), MeCN, Blue LED (2 X 12 W, 440 nm), O_2 (Balloon), 12 h, rt, 89%.

In the presence or absence of varying photocatalysts (viz., rose bengal, eosin B, methylene blue, eosin Y, fluorescence, and rhodamine), visible lights (diffused sunlight, white/blue/ green LED bulbs), and solvents (viz., 1,4-dioxane, acetonitrile, dichloromethane, dimethyl sulfoxide, dimethylformamide, and water) at room temperature under aerial/nitrogen/oxygen

TABLE 1. ATTEMPTED VISIBLE LIGHT INDUCED SYNTHESIS OF **11** TO **12** WITH VARYING CONDITIONS WITH 30% H_2O_2 AND BENZALDEHYDE UNDER THE INFLUENCE OF DIFFERENT VISIBLE LIGHTS AND ATMOSPHERES USING VARYING PHOTOCATALYSTS IN THE PRESENCE OF SOLVENT (S) AT ROOM TEMPERATURE.

entry	photocatalyst	visible light (power)	atmosphere	solvent (1 mL)	time (h)	yield (%)
1	-	sunlight (diffused)	arial (open)	MeCN	8	0
2	-	white LED (2 × 20 W)	O_2	MeCN	8	0
3	rose bengal (3 mol %)	dark	O_2	MeCN	8	0
4	rose bengal (3 mol %)	white LED (2 × 20 W)	O_2	MeCN	4	32
5	rose bengal (5 mol %)	green LED (2 × 20 W)	O_2	1,4-dioxane	4	29
6	eosin Y (3 mol %)	white LED (2 × 20 W)	O_2	MeCN	3	38
7	rhodamine B (3 mol %)	white LED (2 × 20 W)	O_2	1,4-dioxane	8	0
8	rhodamine B (3 mol %)	blue LED (2 × 12 W)	O_2	MeCN	8	34
9	eosin B (3 mol %)	white LED (2 × 20 W)	O_2	1,4-dioxane	8	0
10	fluorescence (3 mol %)	blue LED (2 × 12 W)	O_2	MeCN	8	0
11	methylene blue (3 mol%)	white LED (2 × 20 W)	O_2	1,4-dioxane	8	0
12	methylene blue (5 mol%)	blue LED (2 × 12 W)	O_2	THF	8	0
13	**rose bengal (1 mol %)**	**blue LED (2 × 12 W)**	**O_2**	**MeCN**	**12 h**	**89**
14	rose bengal (1 mol %)	sunlight (diffused)	O_2	MeCN	8	0
15	rose bengal (1 mol %)	blue LED (2 × 12 W)	O_2	1,4-dioxane	8	67
16	rose bengal (1 mol %)	blue LED (2 × 12 W)	O_2	DCM	8	26
17	rose bengal (1 mol %)	blue LED (2 × 12 W)	O_2	DMF	8	0
19	rose bengal (1 mol %)	blue LED (2 × 12 W)	O_2	DMSO	8	34
20	rose bengal (1 mol %)	blue LED (2 × 12 W)	O_2	H_2O	8	0

REACTION CONDITION: KETONE **11** (1GM, 2.15 MMOL), 30% H_2O_2 (0.7 ML, 7.1 MMOL), P-TOLUENE SULPHONIC ACID MONOHYDRATE (PTSA,123 MG, 0.64 MMOL, 30 MOL%), BENZALDEHYDE (455 MG, 4.3 MMOL), MECN (2 ML), O_2 BALLOON, UNDER IRRADIATION BLUE LED (2 × 12 W, 440 NM, CLOSED VESSEL), STIRRED AT RT, 12 H.

presence of benzaldehyde[18] and catalytic PTSA. These experimental results revealed that rose bengal and eosin Y (entry 6), among the photocatalysts tried with, are capable of carrying out the transformation only either in 1,4-dioxane or acetonitrile (entry 15) under the influence of visible light irradiation in an oxygen atmosphere.

The results are summarized in table 1. However, rose bengal (1 mol %) seemed as the best-suited photocatalyst, blue LED (2 × 12 Watt) and acetonitrile came out as the best supporting light source and solvent, respectively, in terms of reaction time and product yield (Table 1, entry 13). This is also to be mentioned herein that the reaction did not undergo in a nitrogen atmosphere, and also in solvents such as dichloromethane, dimethyl sulfoxide, dimethylformamide, and water.

Pleasingly, we were able to establish the optimum reaction conditions for this conversion of **11** to **12** and isolate a pure product of L-dopa derivative (**12**) in very high yield of 89% within 12 h upon irradiating the mixture of **11** (2.15 mmol), 30% hydrogen peroxide (7.1 mmol), benzaldehyde (4.3 mmol) and PTSA (30 mol%) in acetonitrile (1 mL) with blue LED (2 × 12 Watt) in the presence of rose Bengal (1 mol %) as a photocatalyst at room temperature under oxygen atmosphere in a closed vessel (Table 1, entry 13).

A plausible mechanism for the photoinduced oxidation of L-dopa derivative, **12** from **11** via rose Bengal (RB) is proposed (Fig. 4). Initially, under blue light irradiation, RB gets activated to RB*, which transfers photo energy to generate H_2O_2 through an oxygen reduction reaction. Subsequently, H_2O_2 (30 % H_2O_2 is also added externally) undergoes a photo-Fenton like reaction in situ to produce *OH. These radicals then abstract a hydrogen atom from benzaldehyde to form radical PhCO*. The ensuing reaction of radical PhCO* with O_2 produces radical PhCOOO*.19 Finally, PhCOOO* reacts with ketone 11 to form the Criegee adduct intermediate, which further undergoes an intramolecular B-V-rearrangement to produce the Phenol **12** with byproduct benzoic acid after the labile ester functionality is hydrolyzed.

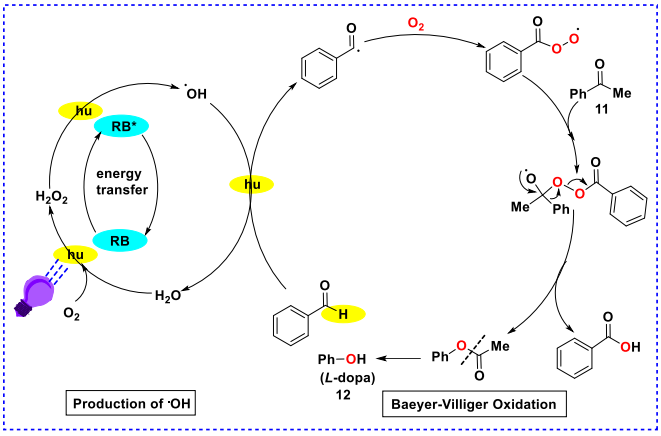


Figure-4. Possible mechanisms of B–V oxidation over Rose Bengal (RB) catalyst.

The L-dopa derivative **12** was obtained as its pure form by flash column chromatography over silica using 15% ethyl acetate in hexane as a colourless oil. The all characteristic ^{1}H-NMR, ^{13}C-NMR, I.R, and mass spectra confirmed its formation. Measurement of optical rotation ([α]D = -15.4, c = 1.1, MeOH) of **12** compared to its exact value ([α]D = -15.1, c = 1.0, MeOH) suggests that no racemization took place during the whole reaction sequences above (Scheme-1&2).

IV. CONCLUSION

In summary, an organic photocatalytic system for Baeyer–Villiger (B–V) reaction to obtain L-DOPA derivatives has been reported, which provides much better yield and mild reaction conditions. It is also making good use of singlet oxygen in the presence of rose bengal as the photosensitizer at ambient temperature (25–28 °C). L-DOPA derivatives are also a valuable scaffold to provide a variety of natural and synthetic compounds of immense biological importance. This present protocol described here may find application in the synthesis of other biologically impotent molecules. The notable advantages of this methodology include the

use of commercially available low-cost starting materials, a low-energy visible light source, cheap and eco-friendly photosensitizers, broader substrate scope, insertion of molecular oxygen, metal-free synthesis, good-to-excellent yields, and energy efficiency. Work will be continued along this direction in my laboratory.

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