EUROPEAN JOURNAL OF BIOMEDICAL AND PHARMACEUTICAL SCIENCES
http://www.ejbps.com

ISSN 2349-8870
Volume: 11
Issue: 8
449-455
Year: 2024

ONE-POT ELECTRO-ORGANIC PRODUCTION OF 5-SUBSTITUTED-3, 4-DIAMINO-1, 2, 4-TRIAZOLES FROM HYDRAZINE HYDRATE AND 1, 3, 4-OXADIAZOLES

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Article Received on 28/06/2024 **Article Revised on 18/07/2024** **Article Accepted on 07/08/2024**

ABSTRACT
A highly facile, efficient and environmentally benign one-pot electro-organic synthesis of 5-substituted- 3, 4-diamino- 1, 2, 4-triazoles from 1, 3, 4-oxadiazoles and hydrazine hydrate is reported in our work. To produce products in good to excellent yields with an eco-compatible greener pathway, the reactions were conducted in the presence of a simple solvent along with a supportive electrolyte. Here electricity is used instead of chemical compound and simple electrodes combination with an electrolyte is utilized in our work. This is one pot, clean and economically favorable protocol.

KEYWORDS: Electro-organic synthesis, 1, 2, 4-Triazoles, Hydrazine hydrates, 1, 3, 4-oxadiazoles, Electrolysis, One pot synthesis.

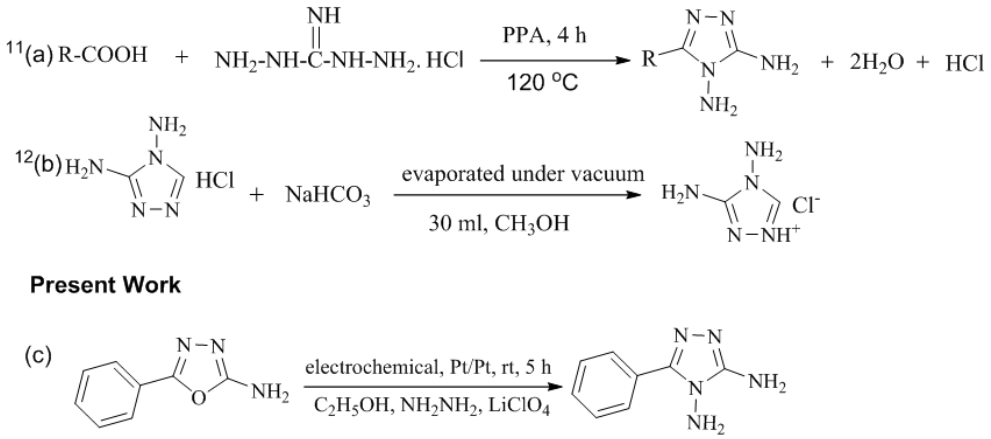
1. INTRODUCTION

The last ten years have witnessed a significant surge in interest in synthetic and therapeutic chemistry due to heterocyclic compounds as final products or as intermediates in the organic synthesis. Heterocyclic compounds have many important biological and pharmacological features.[1] When it comes to five-membered heterocyclic compounds, 5-substituted-3, 4-diamino-1, 2, 4-triazoles have emerged as a key motif in the creation of novel medications. The biological activity of compounds containing 1, 2, 4-triazole cores is wide-ranging and includes anti-bacterial, anti-helmintic,[2] anti-inflammatory,[3] anti-fungal,[4] anti-viral,[5] anti-tubercular,[6] anti-microbial,[7] anti-convulsant,[8] hypo-glycemic,[9] and anticancer[10] properties. Hence, these type of compounds have attracted interest in the field of medicinal chemistry but there is a lack of convenient and combinatorial approaches towards this molecular core.

There are very few methods for synthesizing 5-substituted-3, 4-diamino-1, 2, 4-triazoles that have been published in the literature. Fusco and his colleagues reported in 2011 that they have synthesized these compounds at 120°C in polyphosphoric acid (PPA) utilizing a carboxylic acid and dimethylamine-guanidine monohydrochloride as shown in Scheme 1(a).[11] Nevertheless, a high temperature and polyphosphoric acid (PPA) was needed for this synthesis. On the other hand, Zhang et al. reported the synthesis of four energetic transition metal complexes of 3, 4-diamino-1, 2, 4-triazole in 2016 represented in Scheme 1(b).[12] However this synthesis required expensive transition metal complexes. Therefore, it is still necessary to create straightforward, effective, and a gentle procedure for the synthesis of the triazoles motifs.

Our group mainly focus on green methodologies such as utilization of visible light, electro-synthesis and green catalysis.[13] Electro-organic synthesis has garnered ongoing interest due to its recognition as a diverse and ecologically friendly synthetic method when compared to other classic redox reactions.[14] Utilizing electric current eliminates the need for hazardous and costly reagents and offers a cost-effective and possibly sustainable alternative. It shortens the reaction time of the process, uses less energy and produces fewer waste products. Moreover, the safe and environmental friendly characteristics of electro-organic synthesis with electric current make it a special approach.[15-18]

Considering the foregoing arguments and our ongoing efforts to create simple, effective, and eco-compatible reactions, the first affordable electro-catalytic one-pot synthesis of 5-substituted-3, 4-diamino-1, 2, 4-triazoles from 1, 3, 4-oxadiazole and hydrazine hydrates was anticipated here as Scheme 1(c).

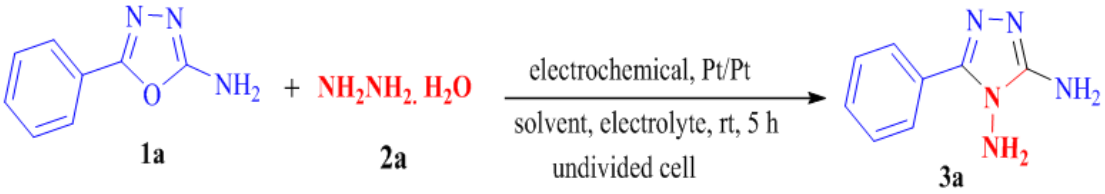


Scheme 1: 5-substituted-3, 4-diamino 1, 2, 4-triazole synthesis.

2. RESULTS AND DISCUSSION

A model reaction comprising 1, 3, 4-oxadiazoles (**1a**, 1 mmol), hydrazine hydrates (**2a**, 1 mmol), lithium perchlorate was utilized as an electrolyte, ethanol and other solvents in order to realize our idea and optimize the reaction conditions (**Table 1**). After treating these compounds with ethanol solution in one-compartment cell with two Pt foils (1 × 1.5 cm^2) as electrodes at room temperature and a constant current density (10 mA/cm^2), the desired product **3a** was obtained in a 92% yield (**Table 1, entry 2**).

Table 1: Optimization of reaction condition for the synthesis of 5-substituted -3, 4-diamino-substituted-1, 2, 4-triazoles.[a]



Entry	Solvent	Electrolyte (equiv.)	Anode/cathode	J (m A/ cm^2)	Yield (%)[b]
1	EtOH	$LiClO_4$ (3)	Pt/Pt	-	0
2	EtOH	$LiClO_4$ (3)	Pt/Pt	10	92
3	EtOH	$LiClO_4$ (3)	Pt/C	10	62
4	EtOH	$LiClO_4$ (3)	C/Pt	10	58
5	EtOH	$LiClO_4$ (2)	Pt/Pt	10	71
6	EtOH	$LiClO_4$ (4)	Pt/Pt	10	92
7	EtOH	-	Pt/Pt	10	n. d[c]
8	EtOH	$LiClO_4$ (3)	Pt/Pt	5	62
9	EtOH	$LiClO_4$ (3)	Pt/Pt	15	60
10	EtOH	NH_4Br (3)	Pt/Pt	10	55
11	EtOH	$KClO_4$ (3)	Pt/Pt	10	54
12	DMSO	$LiClO_4$ (3)	Pt/Pt	10	60
13	DMF	$LiClO_4$ (3)	Pt/Pt	10	52
14	CH_3CN	$LiClO_4$ (3)	Pt/Pt	10	48
15	THF	$LiClO_4$ (3)	Pt/Pt	10	43
16	MeOH	$LiClO_4$ (3)	Pt/Pt	10	44
17	n-PrOH	$LiClO_4$ (3)	Pt/Pt	10	42

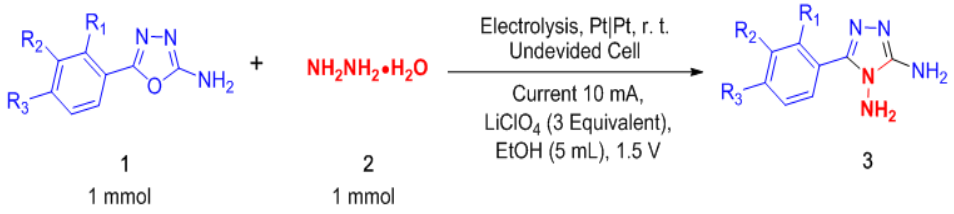
[a]Reaction conditions: 1, 3, 4-Oxadiazoles 1a (1.0 mmol), hydrazine hydrate 2a (1.0 mmol), electrolyte, solvents (30 mL), Pt plate anode, Pt plate cathode, at room temperature.
[b]Isolated yield of pure product 3a.

Pt/Pt was the most efficient combination in terms of production, based on the screening of the electrode materials **(Table 1, entry 2- 4)**. Now the reaction was optimized for a solvent system, EtOH was employed throughout the current investigation because it was discovered to be the best among the all investigated solvents such as DMSO, DMF, CH_3CN, THF, MeOH, and n-PrOH (**Table 1**). Since in the absence of electrolyte, the yield was not observed (**Table 1, entry 7**). Hence, the ideal concentration of the electrolyte $LiClO_4$ (3 mmol) is needed for the reaction process. The yield was much lower when the amount of $LiClO_4$ was decreased from 3 mmol to 2 mmol (**Table 1, entries 2 & 5**), but there was not any effect on the yield of the product if the amount of $LiClO_4$ is increased 3 mmol to 4 mmol (**Table 1, entries 2 & 6**). Other electrolytes were also tried but they were not as effective as $LiClO_4$ (**Table 1, entries 10-11**). At last, the impact of the amount of electricity that was passed was focused in our reaction. The current density of 10 mA/cm^2 (**Table 1, entry 2**) produced the highest yield whereas current density lower than that 5 mA/cm^2 (**Table 1, entry 8**) and higher (15 mA cm-2) (**Table 1, entry 9**) produced lesser yields. Ultimately, it was also discovered that when the reaction was carried out without current, there was no reaction proceed and the starting components were recovered (**Table 1, entry 1**).

Now after optimizing our reaction conditions, the focus of our investigation shifted to the reaction's substrate range as demonstrated in **Table 2**. 1, 3, 4-Oxadiazoles with an electron-donating or electron-withdrawing substituent typically produced excellent yields (75–92%) of 5-substituted-3, 4-diamino-1,2,4-triazoles **3a**–**3l**.

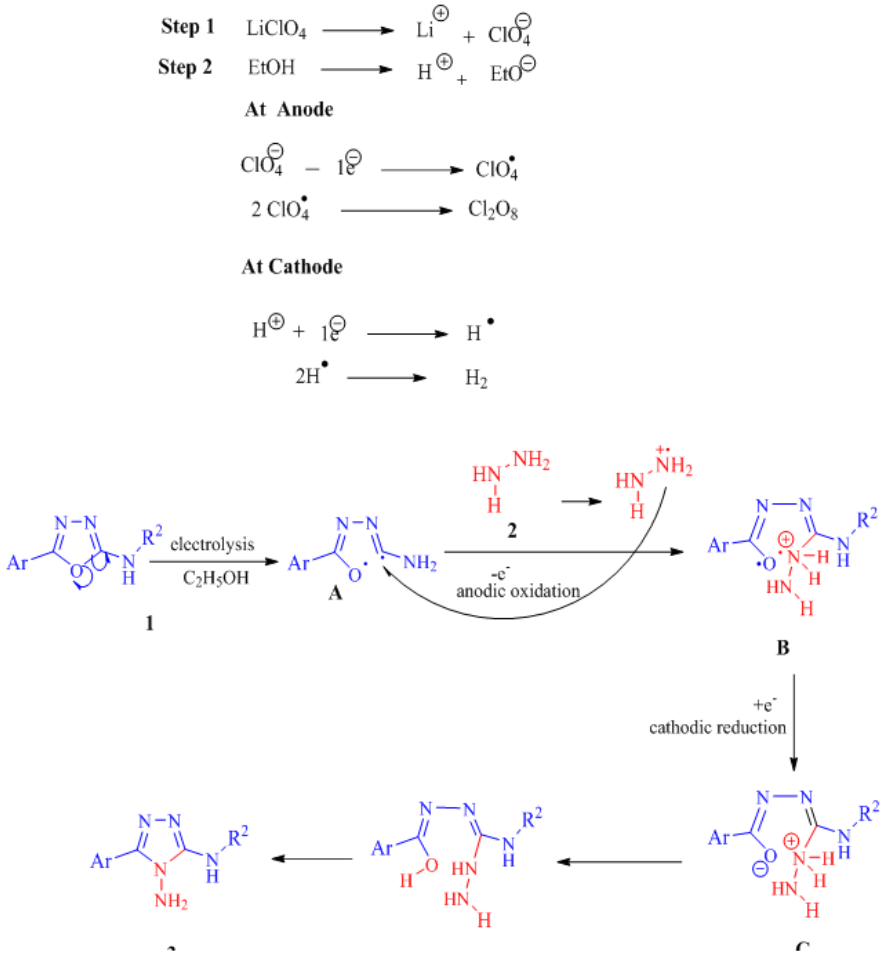
Based on the findings of our experiment and the reports in the literature,[13d, 19] suggests a potential process for 5-substituted-3,4-diamino-1, 2, 4-triazoles' direct synthesis. The single electron transfer (SET) or anodic oxidation of hydrazine hydrate **2** takes place and 1, 3, 4-oxadiazoles **1** undergo electrolysis to generate A. Now anodic oxidized form of hydrazine hydrate and compound A react together to give an intermediate B. This intermediate B then undergo for cathodic reduction to generate C that ultimately convert into final product 3 **(Scheme 2)**.

Table 2: Substrate range for 5-substituted -3, 4-diamino-substituted-1, 2, 4-triazoles via electrochemical synthesis.



Entry	R_1	R_2	R_3	Product	Yield (%)
1	H	H	H	3a	92
2	H	H	NH_2	3b	88
3	H	H	NO_2	3c	89
4	H	H	Cl	3d	90
5	H	H	OH	3e	78
6	H	H	$C(CH_3)_3$	3f	76
7	H	H	OCH_3	3g	77
8	H	H	CH_3	3h	75
9	H	H	OC_4H_9	3i	76
10	Cl	H	H	3j	91
11	H	NO_2	H	3k	90
12	Br	H	H	3l	80

[a]All compounds gave satisfactory spectral (^{1}H NMR, ^{13}C NMR) data.
[b]Yields of isolated pure compounds 3.



Scheme 2: A plausible mechanism for the electrochemical formation of 5-substituted- 3, 4-diamino- 1, 2, 4-triazoles.

MATERIALS

Without additional purification, all commercially available reagents were purchased from commercial vendors. Solvents were kept on molecular sieves after being purified using standard procedures. Glassware that had been oven-dried was used for all reactions, which were conducted in an open environment. In order to concentrate organic solutions, a Buchi rotary evaporator was used. Silica gel (Merck 100–200 mesh) was used for column chromatography, and silica gel GF254 (Merck) plates were used for TLC. Using TMS as an internal reference, ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectra were captured in $CDCl_3$ using a Bruker A VII spectrometer. The chemical shift values were reported in δ (ppm) and every coupling constant (J) is given in Hz (hertz). MS (EI) spectra were captured using a mass spectrometer with double focussing.

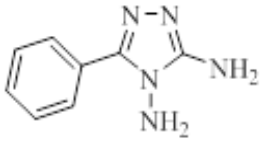
3. EXPERIMENTAL SECTION

3.1. The general protocol for synthesizing 5-substituted-3, 4-diamino-1, 2, 4-triazoles

A mixture of 1, 3, 4-oxadiazoles **1** (1 mmol), hydrazinehydrates **2** (1.0 mmol) and electrolyte $LiClO_4$ (0.3 mmol) in C_2H_5OH (30 ml) was stirred and the mixture of the reaction was moved in to an fitted with an electrochemical cell with a platinum electrode (1 cm^2). Electrolysis was carried out at a constant current density at room temperature. TLC was used to track the reaction's progress using a combination of hexane and ethyl acetate. After following the completion of the reaction, the solid was filtered and residue was purified by recrystallization from EtOH to furnish the desired product.

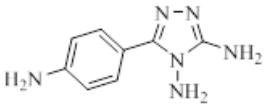
3.2 Experimental Spectral Data for 3(a-l)

3a: 5-phenyl-4H-1,2,4-triazole-3,4-diamine



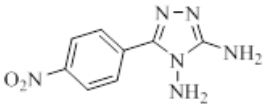
Compound (3a). Isolated as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.48 (s, 2H), 7.48 (s, 2H), 7.50-8.30 (m, 5H aroma); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 120.0, 125.2, 128.0, 130.5, 131.5 (Benzene ring Carbon), 163.5 (1,2,4, triazole ring Carbon). HRMS (EI): calc. for $C_8H_9N_5$ 175.0858, found 175.0860. Elemental Analysis: C, 54.85; H, 5.18; N, 39.98

3b: 5-(4-aminophenyl)-4H-1,2,4-triazole-3,4-diamine



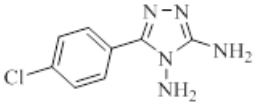
Compound (**3b**). Wheatish White, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.72 (s, 1H), 5.12 (s, 1H), 6.67 (d, 2H *J* = 8.6 Hz), 7.01 (s, 2H), 7.47 (d, 2H *J* = 8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 111.5, 113.7, 126.6, 151.2 (Benzene ring Carbon), 158.4, 163.0 (1,2,4, triazole ring Carbon). HRMS (EI): calc. for $C_8H_{10}N_6$ 209.0967, found 209.0969. Elemental Analysis: C, 50.52; H, 5.30; N, 44.18

3c: 5-(4-nitrophenyl)-4H-1,2,4-triazole-3,4-diamine



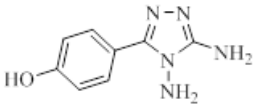
Compound (**3c**). Cream White, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.50 (s, 2H), 7.50 (s, 2H), 7.87 (d, 2H, *J* = 8.6 Hz), 8.44 (d, 2H, *J* = 8.6 Hz), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 124.0, 126.6, 130.0, 132.7, 148.9 (Benzene ring Carbon), 156.0, 164.0 (1,2,4, triazole ring Carbon). HRMS (EI): calc. for $C_8H_8N_6O_2$ 220.0709, found 220.0705. Elemental Analysis: C, 43.64; H, 3.66; N, 38.17; O, 14.53

3d: 5-(4-chlorophenyl)-4H-1,2,4-triazole-3,4-diamine



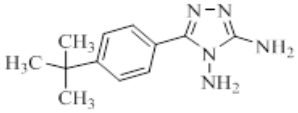
Compound (**3d**). Off-White, ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.47 (s, 2H), 7.48 (s, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.76 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 123.0, 125.9, 135.6 (Benzene ring Carbon), 155.1, 164.4 (1,2,4, triazole). HRMS (EI): calc. for $C_8H_8ClN_5$ 209.0468, found 209.0464. Elemental Analysis: C, 45.84; H, 3.85; Cl, 16.91; N, 33.41

3e: 4-(4,5-diamino-4H-1,2,4-triazol-3-yl)phenol



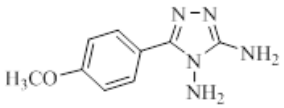
Compound (**3e**). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.26 (s, 2H), 6.99 (d,2H, *J* = 8.6 Hz), 7.02 (s, 2H), 7.63 (d, 2H, *J* = 8.6 Hz), 7.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 116.0, 116.9, 129.8, 158.4 (Benzene ring Carbon), 160.3, 164.1 (1,2,4, triazole ring Carbon). HRMS (EI): calc. for $C_8H_9N_5O$ 191.0807, found 191.0804. Elemental Analysis: C, 50.26; H, 4.74; N, 36.63; O, 8.37

3f: 5-(4-(tert-butyl)phenyl)-4H-1,2,4-triazole-3,4-diamine



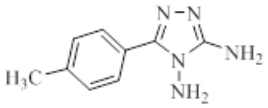
Compound (**3f**). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.31 (s, 9H), 6.44 (s, 2H), 7.10 (s, 2H), 7.44 (d, 2H, *J* = 8.6 Hz), 7.65 (d, 2H, *J* = 8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 31.0, 34.8 (-CH_3), 121.0, 125.0, 126.9, 153.0 (Benzene ring Carbon), 157.5, 163.9 (1,2,4, triazole ring Carbon). HRMS (EI): calc. for $C_{12}H_{17}N_5$ 231.1487, found 231.1484. Elemental Analysis: C, 62.31; H, 7.41; N, 30.28

3g: 5-(4-methoxyphenyl)-4H-1,2,4-triazole-3,4-diamine



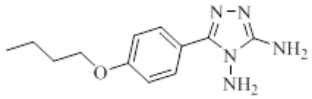
Compound (**3g**). Coconut white, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.60 (s, 2H), 5.58 (s, 2H), 6.20 (s, 2H), 6.15 (d, 2H, *J* = 8.6 Hz), 7.28 (d, 2H, *J* = 8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.0 (O-CH_3), 110.6, 114.1, 120.6, 128.8 (Benzene ring Carbon), 160.0, 164.5 (1,2,4, triazole ring Carbon). HRMS (EI): calc. for $C_9H_{11}N_5O$ 205.0964, found 205.0968. Elemental Analysis: C, 52.67; H, 5.40; N, 34.13; O, 7.80

3h: 5-(p-tolyl)-4H-1,2,4-triazole-3,4-diamine



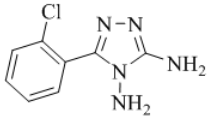
Compound (**3h**). Coconut white, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.30 (s, 2H), 5.59 (s, 2H), 6.37 (s, 2H), 7.12 (d, 2H, *J* = 8.6 Hz), 7.35 (d, 2H, *J* = 8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 24.0 (-CH_3), 123.0, 126.8, 127.5, 131.8, 138.4 (Benzene ring Carbon), 163.8 (1,2,4, triazole ring Carbon). HRMS (EI): calc. for $C_9H_{11}N_5$ 189.1014, found 189.1016. Elemental Analysis: C, 57.13; H, 5.86; N, 37.01

3i: 5-(4-butoxyphenyl)-4H-1,2,4-triazole-3,4-diamine



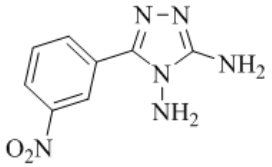
Compound (**3i**). White solid, ^{1}H NMR (CDCl3, 400 MHz) δ: 0.9 (t, *J* = 7.8 Hz, 3H), 1.9 (sextet, *J* = 7.8 Hz, 2H), 2.9 (quintet, *J* = 7.8 Hz, 2H), 3.0 (t, *J* = 7.8 Hz, 2H), 7.73 (d, 2H, *J* = 8.6 Hz), 7.77 (d, 2H, *J* = 8.6 Hz), 7.88 (s, 2H); ^{13}C NMR (CDCl3, 100 MHz) δ: 12.7, 22.0, 49.8, 65.7 (O-butyl), 114.1, 113.8, 149.9, 159.8 (Benzene ring Carbon), 169.7, 177.9 (1,2,4, triazole ring Carbon). HRMS (EI): calc. for $C_{12}H_{17}N_5O$ 247.1433, found 247.1436. Elemental Analysis: C, 58.28; H, 6.93; N, 28.32; O, 6.47

3j: 5-(2-chlorophenyl)-4H-1,2,4-triazole-3,4-diamine



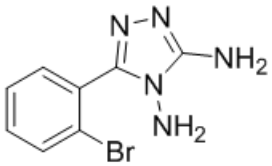
Compound (**3j**). Off-White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.68 (s, 2H), 7.27(s, 2H), 7.47-7.57(m, 2H), 7.75 (d, 2H, *J* = 8.6 Hz), 7.82 (d, 1H, *J* = 8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 123.6, 127.0, 128.4, 130.4, 131.00, 132.0, 132.8 (Benzene ring Carbon), 155.4, 163.3 (1,2,4, triazole ring Carbon). HRMS (EI): calc. for $C_8H_8ClN_5$ 209.0468, found 209.0464. Elemental Analysis: C, 45.84; H, 3.85; Cl, 16.91; N, 33.41

3k: 5-(3-nitrophenyl)-4H-1,2,4-triazole-3,4-diamine



Compound (**3k**). White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.44 (s, 2H), 7.44 (s, 2H), 7.99 (t, 1H, *J* = 7.8 Hz), 8.20 (d, 1H, *J* = 8.6 Hz), 8.32 (d, 1H, *J* = 8.6 Hz), 8.45 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 119.5, 124.7, 125.9, 131.2, 131.3, 148.4 (Benzene ring Carbon),, 155.8, 164.5 (1,2,4, triazole ring Carbon). HRMS (EI): calc. for $C_8H_8N_6O_2$ 220.0709, found 220.0705. Elemental Analysis: C, 43.64; H, 3.66; N, 38.17; O, 14.5

3l: 5-(2-bromophenyl)-4H-1,2,4-triazole-3,4-diamine



Compound (**3l**). Off-White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.69 (s, 2H), 7.29(s, 2H), 7.47-7.59(m, 2H), 7.72 (d, 2H, *J* = 8.6 Hz), 7.85 (d, 1H, *J* = 8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 123.8, 127.2, 128.6, 130.6, 131.5, 132.8, 132.7 (Benzene ring Carbon), 155.2, 163.6 (1,2,4, triazole ring Carbon). HRMS (EI): calc. for $C_8H_8BrN_5$ 254.09, found 254.10. Elemental Analysis: C, 37.82; H, 3.17; Br, 31.45; N, 27.56.

4. CONCLUSION

In conclusion, an ecologically benign and operationally straightforward electrochemical method has been established for 5-substituted-3,4-diamino-1, 2, 4-triazoles' direct synthesis from 1, 3, 4-oxidiazoles and hydrazine hydrates. $LiClO_4$ serves as a supportive electrolyte in the process because this electrolyte proceeds with the strong functional group tolerance and with high efficiency. This synthetic technique generates good to excellent yields in a one-pot procedure under mild circumstances. This protocol is very straight forward and easy to operate.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

ACKNOWLEDGMENTS

We express heartfelt gratitude to the all the esteemed institutions for their resources and contribution for successful completion of the research project. Additionally, we extend sincere appreciation to the SAIF (Spectroscopy and Analytical Instrumentation Facility) for generously providing all the necessary spectroscopic and analytical data crucial to the research and CSIR for the financial support.

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