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세미카바존의 전기적 산화에 의한 2-Amino-5-Substituted-1,3,4-Oxadiazoles 합성

Sanjeev Kumar*
Department of Chemistry, Ishwar Saran College, University of Allahabad, Allahabad-211002, India
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Synthesis of Some 2-Amino-5-Substituted-1,3,4-Oxadiazoles Through the Electrooxidation of Semicarbazone

Sanjeev Kumar*
Department of Chemistry, Ishwar Saran College, University of Allahabad, Allahabad-211002, India
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요 약. 2-Amino-5-Substituted-1,3,4-Oxadiazoles의 합성은 비분할된 셀에서 포텐셜 전기분해의 제어하에 백금전극의 세미카바존 전기적 산화로부터 수행되었다. 이것은 유기화학 합성분야에서 환경적으로 양호한 방법이다. 아세트산 및 아세트니트릴, 무수용매와 리튬 과염소산염 이 전기적 산화에서 전기분해을 위하여 사용 되어졌다. 생성물은 IR, ^{1}H-NMR, ^{13}C-NMR 그리고 원소분석을 통해 구조분석 하였다.

주제어: 전기적 산화, 포텐셜 상수, 전기분해, 전해물, Oxadiazole, 세미카바존, 백금 전극, 친환경 화학

ABSTRACT. The synthesis of 2-amino-5-substituted-1,3,4-oxadiazoles **4** were carried out from the electrooxidation of semicarbazone **3** at the platinum electrode under controlled potential electrolysis in an undivided cell. This is an environmentally benign method in the field of synthetic organic chemistry. The non-aqueous solvents acetic acid and acetonitrile and a supporting electrolyte lithium perchlorate were used for the electrolysis in the electrooxidation. The products were structurally charecterised by IR, ^{1}H-NMR, ^{13}C-NMR and elemental analysis.

Keywords: Electrooxidation, Constant potential, Electrolysis, Electrolyte, Oxadiazole, Semicarbazone, Platinum electrode, Green chemistry

INTRODUCTION

2-Amino-5-substituted-1,3,4-oxadiazoles are of considerable pharmaceutical and material interest which is documented by steadily increasing number of publications and patents. A large number of 1,3,4-oxadiazoles has been discussed in the various literatures because of great anti-microbial,[1] anti-fungal,[2] anti-inflammatory,[3] hypotensive,[4] muscle relaxant[5] and antimitotic activity[6] but all the methods require dangerous reagents specially bromine. the handling of which is very sensitive and various other chemicals which produce environmental hazards.

The development of ecofriendly synthetic method is an example of the recent advances in the technology. It has great importance and is the need of the society.[7] Multistep conventional synthesis produces considerable large amount of environmentally unfavourable wastes mainly due to a series of complex isolation procedure involving expensive and toxic solvents after each step. Thus

the organic synthesis involving electrochemical techniques under suitable solvent and electrolytes are basic requirements.

The electrochemical cyclization has various merits. These reactions can be performed at room temperature and do not require oxidizing chemicals. Application of electricity as a non conventional energy source for activation of reactants in suitable solvents has now gained popularity over the usual homogeneous and heterogeneous reactions. It provides chemical processes with special attributes such as enhanced reaction rate, higher yield of pure products, better selectivity and several ecofriendly advantages.

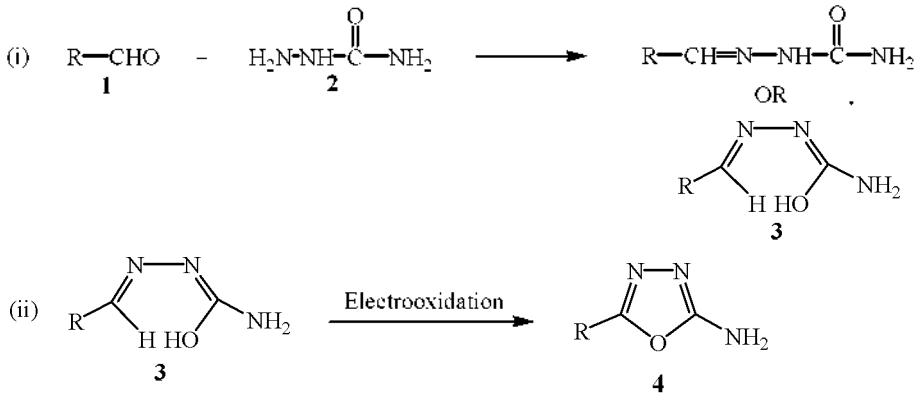
In the continuation of various synthesis,[8] we made an effort as a new method of electrooxidation of the semicarbazone **3** for the preparation of 1,3,4-oxadiazoles which is an example of electrooxidation and we got success in the oxidation of semicarbazone **3.**

RESULTS AND DISCUSSION

1,3,4-Oxadiazole ring systems have a long history of application in the pharmaceutical and agrochemical industries due to their activity. Literature synthesis of oxadiazoles[9] **4** include bromine oxidation of semicarbazide derivative and the cyclodesulfurisation of acylthiosemicarbazide derivative in solution using I_2/NaOH or 1,3-dicyclohexylcarbodimide.[10] as well as mercury-(II)acetate [$Hg(OCOCH_3)_2$] or yellow mercury-(II)oxide.[11] Karen A. Evans and co-workers[12] have reported a similar cyclized product by the chemical method where 2-amino-5-substituted-1,3,4-oxadiazoles were prepared by rapid parallel synthesis in the efficient one-pot preparation using resin-bound reagents. All these methods are usually carried out in different synthetic steps and require high heating and the reagents like bromine or the compounds of the mercury. Not only the handling of these reagents is difficult but also very hazardous to the environment. The high precautions are required during the synthesis from the first step to the last stage of the reaction including the extraction and purification of the products from the reaction mixture.

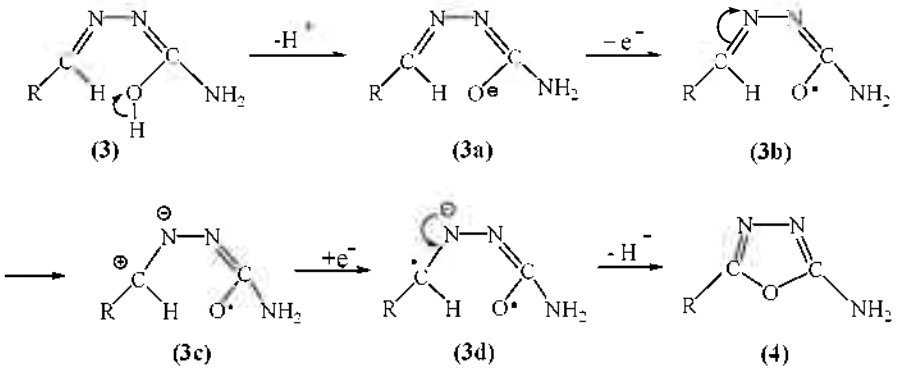
Our objective was to find out a new general ecofriendly synthetic method for the preparation of 1,3,4-oxadiazoles in which the use of above said reagents could be minimised by amount and number both. Keeping these objectives in mind we have synthesized a number of 2-amino-5-substituted-1,3,4-oxadiazoles **4** by electrooxidation of semicarbazone **3**. This electrooxidation gives the oxadiazoles (*Scheme* 1) without requirement of any hazardous reagents. We have used the non aqueous solvents acetonitrile and acetic acid and lithium perchlorate ($LiClO_4$) as an electrolyte that can be handled very easily without major precautions.

The first step represents the deprotonation of **3**



Scheme 1

Mechanism



Scheme 2

to form an anion **(3a)** which after one electron oxidation evolves a free radical **(3b)**. Subsequent second electron reduction from the resonanced form of free radical **(3c)** gives a diradical anion **(3d)**. The coupling of carbon free radical with oxygen free radical completes the ring by making a covalent bond. On loosing a hydride anion in the last step 2-amino-5-substituted-1,3,4-oxadiazole **(4)** is obtained.

Fig. 1. Cyclic voltagram of 2-amino-5-(3-hydroxyphenyl)-1,3,4-oxadiazoles at a glassy carbon electrode (S=π mm^2) in 0.01 M $LiClO_4$ – AN. Scan Rate- 2000 (υ/s).

Fig. 1 presents the cyclic voltammogram obtained from a 0.25 mM solution of lithium perchlorate. The corresponding voltamogram

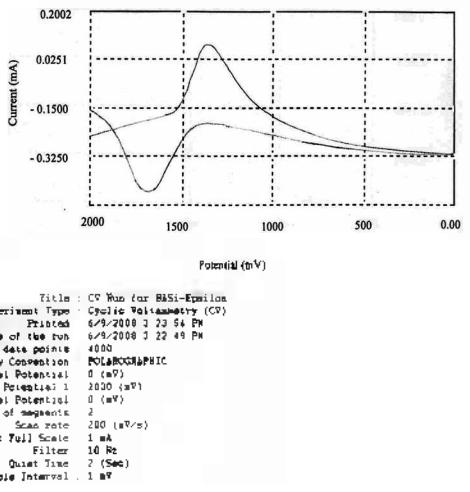


Fig. 1. CV Rn for BASi-Epsilon

Table 1. Current-potential and yield data of electroorganic synthesis of 2-amino-5-substituted-1,3,4-oxadiazoles

Entry	R	Time (Hr)	Applied Potential (V)	Current (A)	% Yield in Acetonitrile	% Yield in Acetic acid
1	3-$(OCH_3)C_6H_4$	3	1.54	0.15	82	89
2	3-ClC_6H_4	4	1.85	0.13	90	96
3	3,4-$Cl_2C_6H_3$	4	1.80	0.12	81	87
4	3-$(OH)C_6H_4$	3	1.55	0.14	88	94
5	C_2H_5	5	2.10	0.25	67	73
6	$CH_3CH_2CH_2$	5	2.22	0.22	65	72
7	$(CH_3)_2CH$	5	2.15	0.19	70	80
8	2,4-$(CH_3)_2C_6H_3$	4	1.70	0.12	81	85
9	CH_2=CH	5	1.80	0.20	75	82
10	2,4,6-$(OCH_3)_3C_6H_2$	4	1.43	0.10	82	87
11	3-CH_3-4-OH-C_6H_3	3	2.00	0.12	80	86

exhibits one anodic peak at 1.446 V *vs* the reference electrode. This peak corresponds to the oxidation of semicarbazone to the product 2-amino-5-(3-hydroxyphenyl)-1,3,4-oxadiazoles.

All the electrolysis were carried out at their corresponding oxidation potential and completed in 3 to 5 h after which no oxidation product was seen to diffuse in the bulk. All the products were solid and coloured and entirely different from the starting compound. The current potential data were recorded at the interval of 15 min which is depicted in *Table* 1.

EXPERIMENTAL SECTION

For constant potential electrolysis, a reaction mixture was prepared by dissolving appropriate amount of substrate and supporting electrolyte in acetonitrile or acetic acid *viz.* **Preparation of reaction mixture for electrooxidation of semicarbazone**: Semicarbazone **3** (1.0 g) was dissolved in acetonitrile (100 mL) and lithium perchlorate (0.106 g) was dissolved in the above solution maintaining the strength of supporting electrolyte 0.001M. **Synthesis of semicarbazone 3:** Semicarbazide hydrochloride (1.0 g) and sodium acetate (1.0 g) **2** was dissolved in water (10 mL) then an aldehyde **1** (0.5 g) was added with continuous stirring. The mixture was left overnight. which gave a solid used as initial compound for electrolysis.

Reagents. The chemicals of high purity were purchased from standard manufacturer such as acetonitrile (Merck), lithium perchlorate (Lobachem) and Chloroform (Merck). The water used was double distilled.

Electrolysis. Preparative scale constant potential electrolysis were performed at room temperature in 250 mL three-electrode cell assembly with platinum plate (flattened sheet of dimension 1.0 cm x 0.5 cm) as working as well as counter electrode and saturated calomel electrode (SCE) as reference electrode.[8] Magnetic stirrer was used for the proper mixing of reaction mixture. The current-potential data given in the *Table* 1 was recorded with the help of potential cum galvanostat. Only a catalytic amount of electricity 5.0-7.5 F mol^{-1} was passed for the electrolysis which is very small in comparison to energy used in other conventional methods.

These experiments were performed in acetonitrile as well as in acetic acid and the products formed were extracted in the similar manner.

Extraction. The product was extracted from acetonitrile to chloroform by simple solvent extraction method.[8] Two-immiscible layers of above solvents were shaken in a seperatory funnel and allowed to settle down. After some time the chloroform layer containing desired product was removed. The extracted chloroform layer was left overnight to evaporate and oxadiazoles **4** were obtained in excellent purity and good yield. As depicted in the *Table* 1 it is observed that the yield in the case of solvent acetic acid is about 5-10 % higher than acetonitrile in almost similar conditions.

Spectral analysis

All melting points were recorded on an electrothermal apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on Bruker DRX 300 (300MHz) FT spectrometer in $CDCl_3$ using TMS as internal reference. Chemical shifts are on parts per million (ppm) relative to tetramethylsilane (TMS) as the internal standard. Microanalysis were carried out in the Elementar Vario EL III. IR spectra in KBr were recorded on a Shimadzu 8201 PC IR spectrophotometer (4000- 400 cm^{-1}).

2-amino-5-(3-methoxy)phenyl-1,3,4-oxadiazole: Dark yellowish needle; mol.wt-191; m.p. 66 °C; IR(KBr, cm^{-1}): υ = 735-860 (o, p-disubstituted benzene), 2815 (O-CH_3), 2850 (aliphatic C-H), 3040 (Ar C-H), 3336 (NH); ^{1}H NMR (300 MHz ; $CDCl_3$/TMS, ppm): δ = 3.73 (s, 3H. OCH_3), 7.25-7.69 (dd, 4H, J = 2.6 and 5.6 Hz, Ar-H), 7.75 (s, 2H, NH); ^{13}C NMR (300 MHz, $CDCl_3$/TMS, ppm): δ = 125.5-137 (6 Ar-C and 2 oxadiazole C), 48.5 (OCH_3). Analysis calcd. for $C_9H_9N_3O_2$: C, 56.54; H, 4.71; N, 21.97. Found: C, 55.94; H, 4.65; N, 21.84.

2-amino-5-(3-chloro)phenyl-1,3,4-oxadiazole: Yellow needle; mol.wt-195.5; m.p. 152-154 °C; IR(KBr, cm^{-1}): υ = 600-800 (Ar-Cl), 735-860 (o, p-disubstituted benzene), 3055 (Ar C-H), 3360 (NH); ^{1}H NMR (300 MHz ; $CDCl_3$/TMS, ppm): δ = 7.00-7.15 (dd, 4H, *J* = 2.6 and 5.6 Hz, Ar-H), 7.75 (s, 2H, NH); ^{13}C NMR (300 MHz, $CDCl_3$/TMS, ppm): δ = 125.5-137.7 (6 Ar-C and 2 oxadiazole C). Analysis calcd. for $C_8H_6N_3OCl$: C, 49.10; H, 3.06; N, 21.48; Cl, 18.15. Found: C, 49.12; H, 3.02; N, 21.35; Cl, 18.10.

2-amino-5-(3,4-dichloro)phenyl-1,3,4-oxadiazole: Yellow needle:, mol.wt-230; m.p. 155-157 °C; IR(KBr, cm^{-1}): υ = 690-810 (m, p-disubstituted benzene), 700-900 (Ar-Cl), 3035 (aromatic), 3341 (NH); ^{1}H NMR (300 MHz ; $CDCl_3$/TMS, ppm): δ = 6.97 (s, 1H, Ar-H), 7.25-7.69 (dd, 2H, *J* = 2.6 and 5.6 Hz, Ar-H), 7.75 (s, 2H, NH); ^{13}C NMR (300 MHz, $CDCl_3$/TMS, ppm): δ = 123-135 (6 Ar-C and 2 oxadiazole C). Analysis calcd. for $C_8H_5N_3OCl_2$: C, 41.73; H, 2.17; N, 18.26; Cl, 30.87. Found: C, 41.53; H, 2.10; N, 17.80; Cl, 30.50.

2-amino-5-(3-hydroxy)phenyl-1,3,4-oxadiazole: Pale yellow needle; mol.wt-177; m.p. 68-70 °C; IR(KBr, cm^{-1}): υ = 735-860 (o, p-disubstituted benzene), 1050 (OH), 3045 (ArC-H), 3350 (NH), 3640 (phenolic); ^{1}H NMR (300 MHz; $CDCl_3$ /TMS, ppm): δ = 7.25-7.69 (dd, 4H, *J* = 2.6 and 5.6 Hz, Ar-H), 7.75 (s, 2H, NH); ^{13}C NMR (300 MHz, $CDCl_3$/TMS, ppm): δ = 125.5-137.7 (6 Ar-C and 2 oxadiazole C). Analysis calcd. for $C_8H_7N_3O_2$: C, 54.23; H, 3.95; N, 23.73. Found: C, 53.88; H, 3.85; N, 23.10.

2-amino-5-ethyl-1,3,4-oxadiazole: Yellow needle; mol.wt-113; m.p. 200-202 °C; IR(KBr, cm^{-1}): υ = 2855 (aliphatic C-H), 1215 (C-C), 3360 (NH); ^{1}H NMR (300 MHz ; $CDCl_3$ /TMS, ppm): δ = 2.49 (m, 2H, J = 7.3 Hz, CH_2), 1.08 (t, 3H, J = 7.3, CH_3), 7.75 (s, 2H, NH); ^{13}C NMR (300 MHz, $CDCl_3$/TMS, ppm): δ = 13.7 (aliphatic C), 128-135.6 (2 oxadiazole C). Analysis calcd. for $C_4H_7N_3O$: C, 42.47; H, 6.19; N, 37.16. Found: C, 42.30; H, 6.15; N, 37.05.

2-amino-5-(n-propyl)-1,3,4-oxadiazole: Yellow colour; mol.wt-127; m.p. 224-226 °C; IR(KBr, cm^{-1}): υ = 2865 (aliphatic C-H), 1210 (C-C), 3261 (NH); ^{1}H NMR (300 MHz ; $CDCl_3$/TMS, ppm): δ = 3.67 (t, 2H, J = 7.1-10.6 Hz, $-CH_2$), 1.27 (t, 3H, J = 6.7 Hz, CH_3), 1.67 (m, 2H, J = 7.1-10.6 Hz, $-CH_2$), 7.75 (s, 2H, NH); ^{13}C NMR (300 MHz, $CDCl_3$/TMS, ppm): δ = 13.7, 15.9, 16.2 (aliphatic C), 128.2-135.6 (2 oxadiazole C). Analysis calcd. for $C_5H_9N_3O$: C, 47.24; H, 7.08; N, 33.07. Found: C, 47.10; H, 6.95; N, 33.00.

2-amino-5-isopropyl-1,3,4-oxadiazole: Yellow colour; mol.wt-127; m.p. 218-220 °C; IR(KBr, cm^{-1}): υ = 2855 (aliphatic C-H), 1200 (C-C), 3360 (NH); ^{1}H NMR (300 MHz; $CDCl_3$/TMS, ppm): δ = 1.33 (d, 6H, J = 6.0-7.8 Hz, CH_3), 2.72 (m, 1H, *J* = 5.5 and 7.0 Hz, $(CH_3)_2CH$), 7.75 (s, 2H, NH); ^{13}C NMR (300 MHz, $CDCl_3$/TMS, ppm): δ = 13.7, 15.9, 16.2 (aliphatic C), 128.2-135.7 (2 oxadiazole C). Analysis calcd. for $C_5H_9N_3O$: C, 47.24; H, 7.08; N, 33.07. Found: C, 47.10; H, 6.95; N, 33.00.

2-amino-5-(2,4-dimethyl)phenyl-1,3,4-oxadiazole: Yellow needle; mol.wt-189; m.p. 76 °C; IR(KBr, cm^{-1}): υ = 2855 (aliphatic C-H), 3030 (ArC-H), 3336 (NH); ^{1}H NMR (300 MHz ; $CDCl_3$ /TMS, ppm): δ = 2.35 (s, 6H, CH_3), δ 6.97 (s, 1H, aromatic), 6.94-7.14 (dd, 2H, *J* = 2.6 and 5.6 Hz, Ar-H), 7.75 (s, 2H, NH); ^{13}C NMR (300 MHz, $CDCl_3$/TMS, ppm): δ = 13.7-14.5 (CH_3), 115-146 (6 Ar-C and 2 oxadiazole C). Analysis calcd. for $C_{10}H_{11}N_3O$: C, 63.49; H, 5.82; N, 22.22. Found: C, 63.21; H, 5.70; N, 26.80.

2-amino-5-ethenyl-1,3,4-oxadiazole: Dark yellow needle; mol.wt-111; m.p. 68 °C; IR(KBr, cm^{-1}): υ = 1646 (C=C), 2868 (aliphatic C-H), 3033 (=C-H), 3261 (NH); ^{1}H NMR (300 MHz ; $CDCl_3$/TMS, ppm): δ = 5.7 (dd, 1H, J = 4.9 Hz, CH_2), 6.7 (d, 1H, J = 4.9 Hz, CH), 5.14 (dd, 1H, J = 5 Hz, CH_2), 7.75 (s, 2H, NH), ^{13}C NMR (300 MHz, $CDCl_3$/TMS, ppm): δ = 13.7 (alicyclic-C), 128-135.7 (2 oxadiazole C). Analysis calcd. for $C_4H_5N_3O$: C, 48.00; H, 5.60; N, 33.60. Found: C, 47.79; H, 5.65; N, 33.61.

2-amino-5-(2,4,6-trimethoxy)phenyl-1,3,4-oxadiazole: Yellow needle; mol.wt-235; m.p. 190-192 °C; IR(KBr, cm^{-1}): υ = 735-770 (o,

p-substituted benzene). 2856.2 (O-CH_3). 2856 (aliphatic C-H). 2927 (Ar C-H). 3444 (NH); ^{1}H NMR (300 MHz ; $CDCl_3$/TMS, ppm): δ = 3.73 (s, 9H, OCH_3), 6.96 (s, 2H, Ar-H), 7.75 (s, 2H. NH); ^{13}C NMR (300 MHz, $CDCl_3$/TMS. ppm): δ = 128.4-129.5 (6 Ar-C and 2 oxadiazole C). 44.2-46.7 (-OCH_3). Analysis calcd. for $C_{11}H_{13}N_3O_3$: C. 56.17; H. 5.53; N. 17.87. Found: C, 56.10; H. 5.43; N. 17.80.

2-amino-5-(3-methyl-4-hydroxy)phenyl-1,3,4-oxadiazole: Yellow needle; mol.wt-191; m.p. 67 °C; IR(KBr. cm^{-1}): υ = 735-860 (m. p-disubstituted benzene). 2850 (aliphatic C-H). 3050 (ArC-H). 3360 (NH); ^{1}H NMR (300 MHz; $CDCl_3$/TMS. ppm): δ = 6.96 (s, 2H. Ar-H), 4.70 (s. 1H. OH). 6.94-7.04 (dd, 2H. *J* = 2.6 and 5.6 Hz, aromatic). 7.75 (s. 2H, NH); ^{13}C NMR (300 MHz, $CDCl_3$/TMS. ppm): δ = 13.7 (CH_3). 114-137 (6 Ar-C and 2 oxadiazole C). Analysis calcd. for $C_9H_9N_3O_2$: C, 56.54; H. 4.71; N. 21.99. Found: C, 56.30; H. 4.52; N. 21.55; Cl. 18.10.

CONCLUSION

It is obvious from the studies that the electroorganic synthesis of 1.3.4-oxadiazole derivatives is an example of electrochemical cyclization by electrooxidation of semicarbazone. It provides a good method for oxadiazole synthesis in good yields which is not so easy to achieve by chemical methods. In the present electrolytic method. electrolysis was carried out at room temperature and no hazardous chemicals were used. Hence the method is ecofriendly and a contribution to green chemistry.

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