International Journal of Enhanced Research in Science, Technology & Engineering
ISSN: 2319-7463, Vol. 12 Issue 1, January-2023, Impact Factor: 7.957

Synthesis of Aminooxadiazoles Using Semicarbazones

N Linganna[1], K K Padmanabha[2]

[1]Associate Professor of Chemistry, Govt. First Grade College, Kuvempu Nagar, Mysore-570023
[2]Associate Professor of Chemistry, Maharani's Science College for Women, Mysore-570005

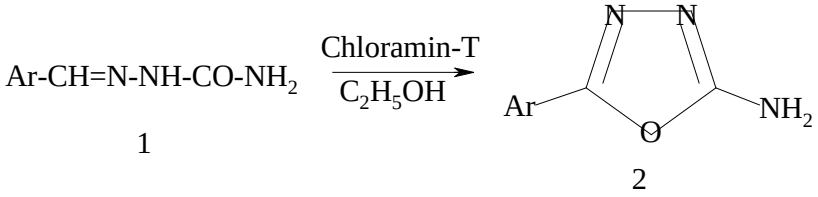
INTRODUCTION

Substituted oxadiazoles have been reported to act as fluorescent whiteners, as herbicides, as funcigides, as hypnitics and sedatives[1]. These compounds also showed analgesic anti-inflammatory, anti-convulsive, diuretic and anti-mitotic activity[2]. Aminooxadiazoles are useful photographic sensitizers and act as muscle relaxants. The usual synthesis of oxadiazoes involves the oxidative cyclisation of hydrazone or semicarbazone[3] with bromine in glacial acetic acid or iodine in aqueous sodium carbonate. Through there are methods for their synthesis, the yields are low (50-70%)[4] or side reactions may predominate[5]. Thus new procedures for the synthesis of aminooxadiazoles remain a topic of interest.

METHODS AND REAGENTS

The procedure for the synthesis of aminooxadiazoles by refluxing an equimolar mixture of semicarbazones with chloramin-T trihydrate in ethanol for 3 hours. In general, aminooxadiazoles were obtained in 80-85% yield.

Structural proof for the aminooxadiazoles were provided by mass, H^1 and C^{13} NMR techniques.



1 2

a. Ar = Ph b. Ar = $4MeoC_6H_4$ c.Ar = 3,4-$(MeO)_2$-C_6H_3 d. Ar = 2,4,6-$(Meo)_3C_6H_2$

Table-1. Yield and physical data of aminooxadiazoles.

Product	Yield (%)	M.P (^{0}C)	Elemental analysis (found)		
			C	H	N
2a	82	238-240	59.6 (59.5)	4.4 (4.3)	26.1 (26.0)
2b	85	242-246	56.5 (56.4)	4.7 (4.6)	21.9 (21.8)
2c	82	213-215	54.3 (54.2)	4.9 (4.8)	19.0 (18.8)
2d	80	197-200	52.6 (52.5)	5.1 (5.0)	16.7 (16.5)

Table-2. Spectral data of aminooxadiazoles.

Product	H^1 NMR ($CDCl_3$) ppm (δ)	C^{13} NMR ($CDCl_3$) ppm (δ)	Mass spectra m/z (relative intensity)
2a	3.34 (bS, 2H, NH_2) 7.52 (m, 2H, ArH) 7.80 (m, 3H, ArH)	124.3 (s, C1) 124.92 (d, C-2, 6) 129.08 (d, C-3, 4) 157.24 (s, C-5) 163.75 (s, C-2)	162 (M+1, 100) 161 , M+, 81)
2b	3.36 (bS, 2H, NH_2) 3.82 (s, 3H, OMe) 7.15 (d, 2H,3,5-H) 7.72 (d, 2H, 2, 4 –H)	55.31 (q, OMe) 114.61 (d, C-3, 5) 116.95 (s, C-1) 126.94 (d, C-2, 6) 157.29 (s, C-5) 160.79 (s, C-4) 163.47 (s, C-2)	192 (M+1, 100) 191 , M+, 12)
2c	3.33 (bS, 2H, NH_2) 3.823(s, 6H, OMe) 7.12 (m, 2H,ArH) 7.31 (m, 1H, Ar –H)		222 (M+1, 100) 221, M+, 9)
2d	3.36 (bS, 2H, NH_2) 3.38 (s, 3H, OMe) 4.02 (s, 6H, OMe) 7.02 (s, 2H, Ar –H)		252 (M+1, 100) 251, M+, 10)

Experimental procedure

NMR spectra were recorded on a Bruker MHz spectrometer in $CDCl_3$ solution. H^1 NMR spectra were measured at 300 MHz, TMS was used as an internal standard and chemical shifts are expressed in ppm (δ scale). C^{13} NMR spectra were measured at 75 MHz and the values are in ppm down field from TMS. Mass spectra were obtained on a Finnigan mass spectrometer. Chromatographic separations were carried out on silica gel column using chloroform/acetone (7:1) as eluent.

Preparation of aminooxadiazoles

The mixture of semicarbazone (1b) (2 g) and CAT.$3H_2O$ (3g), in ethanol was refluxed with stirring for 3 hours. The sodium chloride formed in the reaction was filtered off and washed with ethanol the combined filtrate and washings were evaporated in vacuum and the residue was extracted with

10% HCl and washed thoroughly with dichloromethane. The aqueous layer on neutralization with 10% NaOH (15 mL) gave 2b as a white solid which is washed and dried. Recrysatllisation from ethanol gave 1.67 g of aminooxadiazole.

REFERENCES

1. Hill J , "comprehensive heterocyclic chemistry, Katritzky, A R, ed.al , 1984, vol-6, p-427.
2. Thomas J, Ger Offen, 1974, Vol-2, 403, 357, Chemical abstract, 1974, Vol-81.
3. Hiremath S P, Shivaramaiah, Rajshekar K and Purohit M G, Indian .Journal of Chemistry, 1990, vol-29B, P-1118
4. Blankenstein C and Mockel K, Z Chem, 1962, Vol-2, P-69
5. Hetzheim A and Mockel K, Advanced heterocyclic chemistry, 1966, Ed.7, P-187.