Indian J.Sci.Res. 7(2): 229-231, 2017 ISSN: 0976-2876 (Print)
ISSN: 2250-0138(Online)

$AICI_3$ CATALYSES ONE-POT SYNTHESIS OF BENZOXADIAZEPINES DERIVATIVE

ARUN KUMAR PATEL[1]

Department of Chemistry, Rashtriya P.G. College Jamuhai, Jaunpur, U.P., India

ABASTRACT

Benzoxadiazepine derivatives have been synthesized in solvent- free condition from o-phenelyenediamine and aldehydes in the presence of AICI; as catalyst. This method is one-pot synthesis and applicable to aromatic and aliphatic aldehyde to substituted o-phenelyenediamine without significant difference.

KEYWORDS: AIC13 Aldehydes, Benzoxadiazepines, Solvent- Free Reaction

Benzoxadiazepines have recently attracted attention as an important class of seven membered heterocyclic compounds fused with benzene ring in the field of drugs and pharmaceuticals. These compounds are widely used as CNS stimulantsl-2 muscle relaxants', tranquilizers, anticonvulsants, pesticides and insecticides", antibacterial and anti-inflammatory agents. The synthesis of benzoxadiazepines has attracted the attention of synthetic organic chemistry since last one decade. However only few methods are available for synthesis of benzoxadiazepines in literature (Singh, G. et al. Abstr. 1996, 124, 86970e). (Reddy, P.S.N.;Reddy et al. 1996). (El-Rady et al. 2002).

Generally, benzoxadiazepines were synthesized by the condensation of ophenylenediamine with aldehydes-. We have employed AICI; as a selective reagent for cyclodehydration of N,N'-diacylhydrazine resulting in the formation of 1,3-oxazoles'. Encouraged by excellent yield obtained for 1,3-oxazoles, we further employed AlCl3 as selective reagent for cyclodehydration of N,N-diacyl-1,2-phenylenediamines. We envisaged that cyclohydration of N,N'-diacyl derivative with AlCl3 would lead to formation of 2,4disubstitued-3,1,5-benzoxadiazepines 3a-g Petigara, R.B et al. 1979.

A typical reaction procedure involves the addition of 1,2-phenylenediamine 1, to the aldehyde 2 add AlCl3 methylcyanide refluxed for 2-3 hrs. AlCl3 is a Lewis acid catalyst used in a wide variety of applications, such as in mild dehydration of acetoylchloride to alkenes, in Fredal-croftacylation, in cleavage of ethers in THP protection of alcohols in rearrangement of epoxides to carbonyl compound in reaction of allyltin reagents with aldehyde and ketones etc. Here in we wish to disclose a novel protocol for the rapid synthesis of a variety of biologically significant benzoxadiazepines using a catalytic amount of AlCl3 under extremely mild solvent - free condition the reaction was carried out in heat at room temperature for 30 minutes Bristol, J.A et al. 1977.

The result are summarized in table-1.

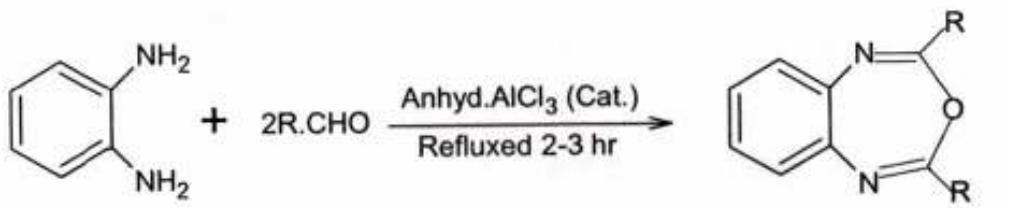
RESULTS AND DISCUSSION

In our initial study we use aldehydes as a respective reagent in order to optimize the reaction conditions. For the synthesis of 2,4-disubstitued-3,1,5-benzoxadiazepines 2 moles of aromatic, aliphatic and Q, B-unsaturated aldehydes and substituted phenylenediamine react without any significant difference to give the corresponding benzoxadiazepines in good yield. Best results were obtained using 0.5 equivalent of AICI: lower loading resulted in lower yields, while higher loading did not increase product yields significantly. The scope and generality of this procedure is illustrated with respect to various o-phenylenediamine and a wide range of aldehydes and the results are presented in table 1. This method offers several advantages such as high conversions, shorter reactions times, cleaner reaction profiles , solvent-free conditions and simple experimental and work up procedure Petigara, R.B et al.1977 .

In recent year solvent-free methods are used in the form of microwave irradiation but a simple work-up procedure, mild reaction condition and very good yields make our methodology a valid contribution to the exiting process in the field of benzoxadiazepines derivatives synthesis Lee et al. 1992.

---

[1]**Corresponding Author**



Scheme 1

AlCl$_3$ promoted synthesis of benzoxadiazepines

Table 1: Isolated 2,4-disubstitued-3, 1, 5-benzoxadiazepines 3 from o-phenylenediamine

Product	R	M.P.	Yields
a	CH_3	71-73 ^{0}C	81%
b	C_6H_5	101-103 ^{0}C	89%
C	4-Cl-C_6H_4	145 ^{0}C	92%
D	4-MeO-C_6H_4	125 ^{0}C	91%
E	4-O_2N-C_6H_45	180 ^{0}C	88%
F	4-2-C_5H_4N	97-98 ^{0}C	91%
g	4-C_5H_4N	90 ^{0}C	89%

Experimental Section

Melting points were determined in open capillaries on an electrically heated melting point apparatus and are uncorrected. Progress of the reaction and purity of the compounds were monitored by thin layer chromatography (TLC), which was performed on silica gel G (Merck) and compounds were detected with iodine vapours. IR spectra were recorded on a Perkin-Elmer model 137 spectrometer in KBr pellets Mazurkiewicz et al.1988 'H-NMR (200MHz) spectra were recorded on a Perkin-Elmer model R-32 spectrometer in suitable solvents using TMS as an internal standard. 13 C-NMR spectra were recorded on Bruker AVANCE DPX 200 MHz using TMS as an internal standard. MS spectra were recorded Joel-JMS-D300 spectrometer. Elemental analyses were obtained for all the compounds Tandon et al. 2001.

Synthesis of 2,4-Disubstituted-3,1,5-benzoxadiazepines 3a-g

A mixture of O-phenylenediamine (1 mmole) and AlCl3 (0.5mmole) in CH3CN (25ml)and was added aldehyde (2.2 mmole). Then the reaction mixture was refluxed to complete the reaction as fallowed by TLC. After the completion of the reaction the mixture was brought to RT and poured into ice-cold water. The crude product thus obtained was filtered and purified by recrytallization from EtOH to afford in 90% yields. The crude compounds were purified by silica gel column chromatography using CH2Cl2-MeOH (95:5) as eluent.

2,4-Dimethyl-3,1,5-benzoxadiazepine (3a) :

Solid (Light Yellow Powder); Cryst. with Benzene-Hexane; Yield: 81 %; mp: 71-73 °C (lit. 70-72 °C); IR (nujol mull, cm*') 1703 (C=N), 1121 (C-O-C); 'H-NMR (CDC13, ppm): 7.12 (s, 6H, 2CH3); 13C-NMR: 8 18.8, 42.3, 123.3, 128.5, 164.0; MS (El): m/z = 174 [MT]; Elemental analysis: Calcd. For C10H10N20 : C, 68.95; H, 5.79; N, 16.08; Found: 0,70.02; H, 5.83; N, 16.92.

2,4-Diphenyl-3,1,5-benzoxadiazepine (3b):-

Solid (Pink Powder); Cryst. with EtOH; Yield: 89 %; mp: 101-103 °C (lit. 100-101 °C); IR (KBr, cm') 1665 (C=N), 1023 (C-O-C); 'H-NMR (CDC1z, d ppm):

7.20-7.69 (m, 14H, ArH); 13C-NMR: 8 46.5, 123.5, 128.7, 128.9,129.3, 130.8, 131.3, 164.0; MS (El): m/z = 298 [MT]; Elemental analysis: Calcd. For C20H14N20 : C, 80.52; H, 4.73; N, 9.39; Found: C,80.70; H, 4.87; N, 9.52.

2,4-Bis(4-Chlorophenyl)-3,1,5-benzoxadiazepine (3c) :

Solid (White Powder); Cryst. with EtOH; Yield: 92 %; mp: 145 °C ; IR (KBr, cm*') 1663 (C=N), 997 (C-O-C); 'H-NMR (CDC13, 8 ppm): 7.29-7.65 (m, 12H, Ar-H); ">C-NMR: 8 46.6, 123.3, 128.4, 129.2, 129.7, 130.5, 136.1, 164.0; MS (El): m/z = 367 [MT]; Elemental analysis: Calcd. For C20H12N20: C, 65.41; H, 3.29; N, 7.63; Found: C,65.92; H, 3.40; N, 8.04.

2,4-Bis(4-Methoxyphenyl)-3,1,5-benzoxadiazepine (3d) :

Solid (Pale Yellow Powder); Cryst. with EtOH; Yield: 91 %; mp: 125 °C ; IR (KBr, cm*') 1681 (C=N), 1025 (C-O-C); 'H-NMR (CDC13, 8 ppm): 3.86 (s, 6H, OCH3); 6.94 (m, 8H, ArH); 7.85 (m, 4H, Ar-H); C-NMR: 8 56.1, 114.5, 123.3, 128.5, 130.2, 146.3, 164.0, 164.3; MS (El): m/z = 358 [MT]; Elemental analysis: Calcd. For C22H18N203 : C, 73.74; H, 5.02; N, 7.82; Found: C, 73.95; H, 5.06; N, 7.95.

2,4-Bis(4-Nitrophenyl)-3,1,5-benzoxadiazepine (3e):

Solid (Yellow Powder); Cryst. with Benzene; Yield: 88 %; mp: 180 °C ; IR (KBr, cm') 1677 (C=N), 1018 (C-O-C); 'H-NMR (CDC13, 8 ppm): 7.53 (m, 4H, Ar-H); 7.95-8.18 (m, 8H, Ar-H);">C-NMR: 8 46.8, 50.8, 123.4, 123.8, 128.4, 129.8, 137.2, 164.0; MS (EI): m/2 = 388 [M']; Elemental analysis: Calcd. For C20H12N4Os : C, 61.86; H, 3.11; N, 14.43; Found: C, 61.90; H, 3.13; N, 14.59

2,4-Bis(2-Pyridyl)-3,1,5-benzoxadiazepine (3f):

Solid (Brown Powder); Cryst. with Benzene; Yield: 91 %; mp: 97-98 °C ; IR (KBr, cm 1 1681 (C=N), 1020 (C-O-C); 'H-NMR (CDC13, 8 ppm): 7.69-8.18 (m, 8H, Pyridyl-H); 7.48 (m, 4H, Ar-H); ">C-NMR: 8 42.46, 123.5, 124.0, 128.3, 135.7, 150.0, 152.5, 164.0; MS (El): m/s = 300 [MT]; Elemental analysis: Calcd. For C18H12N40 : C, 71.95; H, 4.04; N, 18.67; Found: C, 72.13; H, 4.65; N, 18.98.

2,4-Bis(4-Pyridyl)-3,1,5-benzoxadiazepine (38) :-

Solid (Light Brown Powder); Cryst. with Benzene; Yield: 89 %; mp: 90 °C ; IR (KBr, cm 1) 1681 (C=N), 1020 (C-O-C); 'H-NMR (CDC13, 8 ppm): 8.01-8.85 (m, 8H, Pyridyl-H); 7.48 (m, 4H, Ar-H); 13C-NMR: 8 42.46, 123.3, 124.0, 128.3, 135.2, 150.0, 152.5, 164.0; MS (EI): m/z = 300 [MT]; Elemental analysis: Calcd. For C18H12N40: C, 71.95; H, 4.04; N, 18.67; Found: C, 72.11; H, 4.52; N, 18.95.

ACKNOWLEDGEMENT

Authors are thankful to Central Drug Research Institute (CDRI), Lucknow for providing spectral data and elemental analysis. Authors are also thankful to head deportment of chemistry for providing laboratory and library facilities .

REFERENCES

Petigara R.B. and Yale H.L., 1979. U.S. Patent, 4, 134, 975. 2

Bristol J.A. and Yale H.L., 1977. U.S. Patent 4, 062, 852.

Petigara R.B. and Yale H.L., 1975. U.S. Patent 3, 856, 801, 1977; Chem. Abstr. 82, 31362s.

Singh G., Singh C. and Kaur H., 1995. Asian J. Chem., **7**: 735. Chem. Abstr. 1996, 124, 86970e.

Reddy P.S.N., Reddy P.P., Padmaja K., Shailaja G. and Reddy D.S., 1996. Ind. J. Chem., 35B, 1110.

El-Rady E.A.J., 2002. Heterocycle. Chem. 39,1109.

Lee K.J., Kim S.H., Kim S. and Cho Y.R., 1992. Synthesis, 929.

Mazurkiewicz R., Monatash. Chem. 1988, 119, 1279.

Tandon V.K. and Chhor R.B., 2001. Synth. Commun. 31,1727.