A Modified-One Pot Synthesis of Diaminoglyoxime

Kakanejadifard, Ali*+

Department of Chemistry, Faculty of Science, University of Lorestan, P.O. Box 465, Khoramabad, I. R. IRAN.

Farnia, S. Morteza and Najafi, Golamreza

Department of Chemistry, Faculty of Science, Tehran University, Tehran, I. R. IRAN.

ABSTRACT: *The one pot reaction of glyoxal and hydroxylamine hydrochloride in aqueous sodium hydroxide was found to be a safe and inexpensive method for the preparation of diaminoglyoxime. By increasing stoichiometric ratio of the hydroxylamine hydrochloride and decreasing the solvent volume, the product yield increased considerably (~ 70%).*

KEY WORDS: *Glyoxime, Diaminoglyoxime, Diaminofurazan, 1,2,5-oxadiazole, Furozanring.*

INTRODUCTION

The furazan ring has been found to be a useful substructure for the design of new high density, high-energy materials composed exclusively of carbon, hydrogen, nitrogen and oxygen atoms. The diamino-furazan 1 has been shown to be a useful precursor for the construction of high-energy furazan derivatives 2 and 3.

There are several reports in the literature, describing the methods for the synthesis of 1 and 5. However, these procedures require the use of obscure starting materials and hazardous or expensive reagents [4-9]. In 1995, the synthesis of 1 was achieved in two steps from the readily available glyoxime 4.

The preparation of 1 has been limited by the availability of precursor diaminoglyoxime 5. The burning rates of composite rocket propellants are known to decrease when small amounts of 5 and 1 are added [1-3].

The key intermediate 5 was prepared from the reaction of 4 and hydroxylamine hydrochloride in an alkaline aqueous sodium hydroxide solution with 60%yield at 90°C [9-12], where, 4 was obtained from the reaction of glyoxal and hydroxylamine hydrochloride in aqueous sodium hydroxide with 60% yield [13].

In this work, we developed a modified one pot synthesis based an the available reagents (hydroxylamine hydrochloride, glyoxal). By increasing the hydroxylamine hydrochloride in stoichiometric ratio and decreasing the solvent volume, the yield of reaction increased considerably (69-71%). This procedure represents improvement over the methods previously reported in that the diaminoglyoxime 5 results from the commercially available reagents in one pot, with high yield and low cost.

Synthesis of diaminoglyoxime(5)

To a colorless stirred solution of hydroxylamine hydrochloride (27.8gr, 0.4 mole) , aqueous sodium

* *To whom correspondence should be addressed.*
+ *E-mail : kakanejadi.a@ lu.ac.ir*
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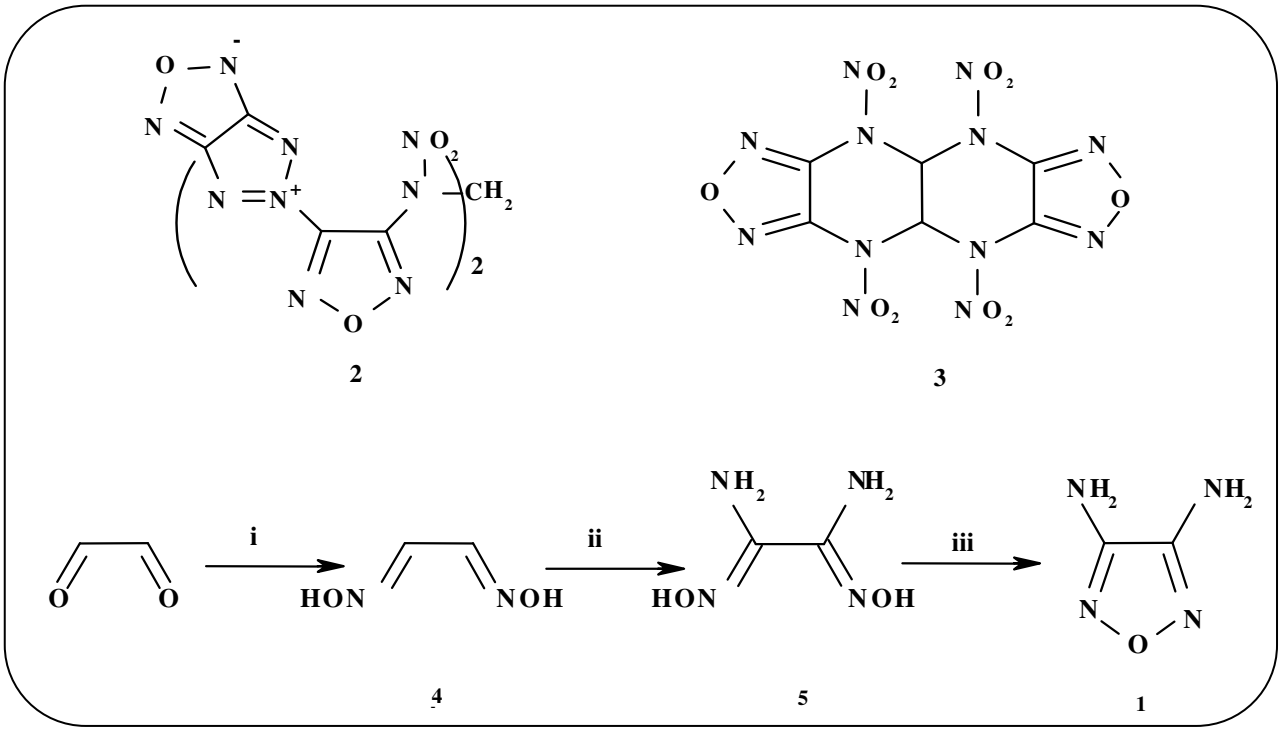
hydroxide(80 ml, 5 M) in a 250 ml round bottom flask , was added glyoxal (11.6gr of 40% aqueous solution , 0.08 mole). After 30 minutes, the flask was fitted with a condenser and heated at 90-95 °C for 5 hours. The yellow solution was allowed to cool to 5°C. The colorless crystalline were then filtered and the filtrate concentrated to get residual precipitates. The colorless crystalline washed with 10 ml cold water and dried to give 7.18 gr (69-71%) of crude product, mp 197-199°C (dec), lit 203-205°C[10]. Recrystallization from distilled water gave crystals of 5, mp 203-203.5°C. IR (KBr) cm^{-1}; 3476, 3376 (NH_2) 2828-3196 (OH), 1650.4, 1573.6, 1445.6,954.4, 940.^{1}H-NMR (DMSO -d_6) δ; 5.19 (bs, 4H, NH_2), 9.77(s, 2H, OH). ^{13}C-NMR (DMSO-d_6) δ; 145.22.



Reagent i : 2NH$_2$ OH HCl / NaOH , 5 °C
ii : 2NH$_2$ OH HCl / NaOH ,95 °C
iii : KOH / -H$_2$O , 170 °C

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