Synthesis of N, N´3, 4-Dialkylamino-1, 2, 5-Oxadiazoles

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ABSTRACT: *N, N´-3, 4-di(methylamino)-1, 2, 5-oxadiazole (1f) was prepared by dehydration of N, N´-3, 4-di(methylamino)glyoxime (2f) in aqueous potassium hydroxid at 170-180 ˚C. Under similar conditions N, N´-3, 4-di(benzylamino)-1, 2, 5-oxadiazole (1c) and N, N´-3, 4-di(isopropylamino)-1, 2, 5-oxadiazole (1e) were not obtained, but, N, N´-3, 4-di(ethylamino)-1, 2, 5-oxadiazole (1g) was appeared with small amount.*

KEY WORD: *N, N´-3, 4-di(methylamino)-1, 2, 5-Oxadiazole, Dehydration, N,N´-disubstituted Diaminoglyoxime, Dichloroglyoxime*

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 [1-4]. However, the preparation of N, N´-3, 4-disubstituted diamino-1, 2, 5-oxadiazoles (1) have been limited by the availability of recursor diaminoglyoximes (2). The burn rate of composite rocket propellants is known to decrease when small amounts of 1 and 2 are added [5-7]. The 3,4-diamino-1, 2, 5-oxadiazole (1a) and N, N´-3, 4-di(phenylamino)-1, 2, 5-oxadiazole (1b) were obtained by dehydration of N,N´-disubstituted diaminoglyoximes (2a,2b) in an alkaline aqueous solution [2,8-10]. Fischer has prepared N, N´-3, 4-disubstituted diamino-1, 2, 5-oxadiazoles (1c-e) by condensation of 1a with aldehyde or ketons prior to reduction by sodium borohydrid (Scheme 1)[11]. To the best of our knowledge, there is no report on the synthesis of N, N´-3, 4-dialkylamino-1, 2, 5-oxadiazole by dehydration method. In this paper, we report results obtained in the synthesis of N, N´-3, 4-dialkylamino-1, 2, 5-oxadiazoles.

RESULTS

The reaction of dichloroglyoxime with alkylamines (methylamine, isopropylamine and benzylamine) leads to N, N´-di(alkylamino)glyoxime (2c-f). The N, N´-3, 4-di(methylamino)-1, 2, 5-oxadiazole (1f) was prepared bydehydration of N, N´-3, 4-di(methylamino)glyoxime (2f) in aqueous potassium at 170-180 ˚C. Compounds 1c-e were not obtained under similar condition, but a small amount of an oily product of 1g was appeared (Scheme 2). In spite of applicability of the Fischer's method [11]

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for preparation of 1c-e, any effort for synthesis of 1f and 1g leads to unsatisfactory results. In the other hand, the dehydration method, which, is suitable for synthesis of 1a and 1b, it seems, to be a prefer method for preparation of 1f.

EXPRERIMENTAL

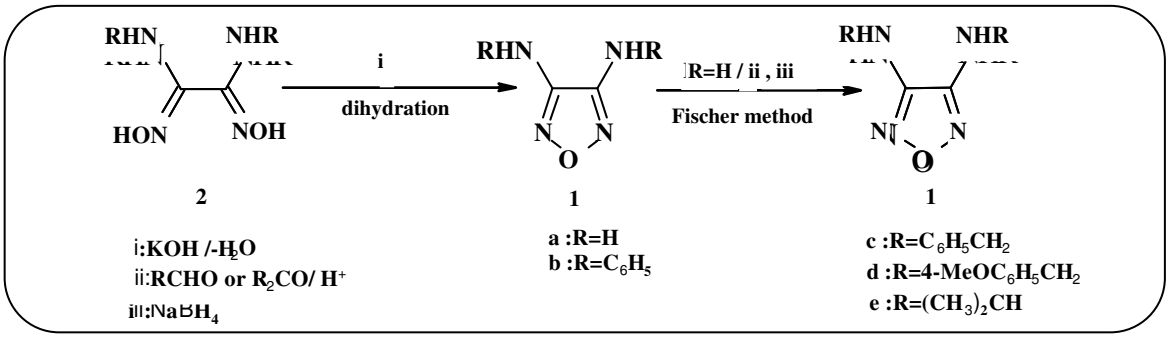
All chemicals were purchased from *Merck* Company. Melting points were determined with an Electrothermal 9200 apparatus and uncorrected. IR spectra were recorded on a Shimadzu 460 spectrometer. NMR spectra were recorded with a Brucker DRX- 500 AVANCE instrument. Mass analysis of the product was conducted with a Finigan Matt 8000 GC-Mass instrument. Elemental analysis were carried out with a C, H, N, O Rapid-Heraeus apparatus

Preparation of N, N′-di(methylamino)glyoxime (2f)

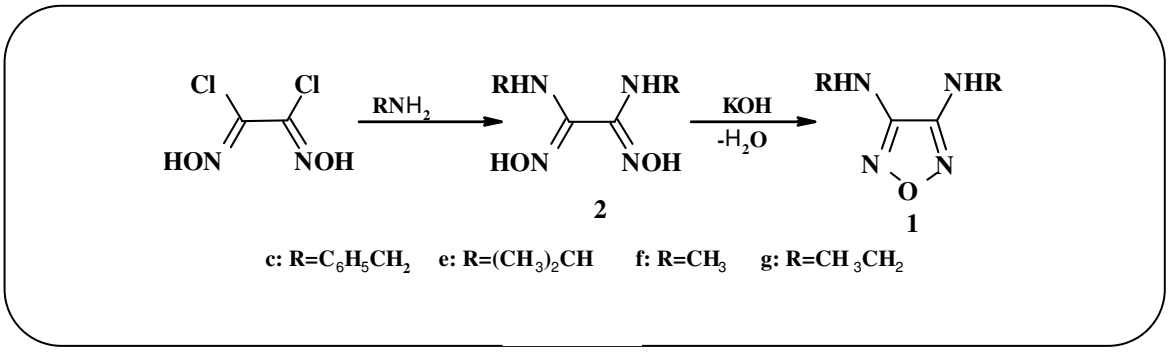
To a stirring solution of 1.57g dichloroglyoxime (10 mmole) in 40 ml of distilled water, 3.1 g of methylamine (40 mmole, aqueous solution of 40%) at 0 ˚C was added in one portion. The reaction mixture was stirred for 30 min. The brown solution was alkalized with potassium hydroxide to pH > 8 and placed in the refrigerator for 5 days. The pure white crystals of 2f was collected by filtration; 0.26g (17.8% yield, mp 225.7-227.1 ˚C). IR (KBr) cm^{-1}, 3400 (NH), 3650-2600 (OH), 1680, 1655 (C=N), 1480, 908(N-O). M/z, 146. Compounds 2c-e were prepared under similar condition (2c, yield 92%, mp 147-148 ˚C. 2e,yield 65%, mp 152-153 ˚C)

Synthesis of N, N 3, 4′-di(methylamino)-1, 2, 5-oxadiazole (1f). Method A

A suspension of 1.46g (10 mmole) of 2f in 20 ml aqueous potassium hydroxide (2M) was placed in a stainless steel reactor. The reactor was closed and placed in an oil bath preheated to 170-180 ˚C and maintained at that temperature for 2 hours. The reactor was cooled, then placed in an ice bath for 2 hours and opened carefully. The mixture extracted into ethyl acetate (3×20) and dried (magnesium sulphate). Solvent was removed under reduced pressure to yield a brown oily solid, which was recrystallized from ethyl acetate/hexane to afford 0.46 g of the desired material as



Scheme (1)



Scheme (2)

white needles (36% yield, mp 104.7-106.2 ˚C). IR (KBr) cm^{-1}: 3408,3350(NH), 1627, 1606, 1522, 1282, 1258, 986(N-O). ^{1}H-NMR (acetone-d_6) δ: 5.07 (bs, 2H, NH), 2.87-2.89 (d, 6H, J=5.08Hz, CH_3). Upon addition of D_2O to NMR sample, the NH signal disappeared and methyl protons signal collapsed into a singlet. ^{13}C- NMR (acetone-d_6) δ: 150.93, 30.29. EI-Mass spectrum, m/z, $129(M+1)^+$, $128(M^+)$. Calculated for $C_4H_8N_4O$: C, 37.50;. H, 6.25; N, 43.75. Found: C, 37.48; H, 6.24; N, 43.69. Compounds 1c-e and 1g were not obtained under similar condition.

Method B

To a stirred solution of 1.57g dichloroglyoxime (10 mmole) in 40 ml of distilled water, 3.1 g of methylamine (40 mmole, aqueous solution of 40%) at 0 ˚C was added in one portion. The reaction mixture was stirred for 30 min and 3.36g of potassium hydroxide were added. This mixture was placed in a stainless steel reactor. The reactor was closed and placed in an oil bath preheated to 170-180 ˚C and maintained at that temperature for 2 hours. The reactor was cooled by immersion in ice bath for 2 hours and opened carefully. The mixture was extracted into ethyl acetate (3×20) and dried (magnesium sulphate). Solvent was removed under reduced pressure to yield a brown oily solid that was recrystallized from ethyl acetate/hexane to afford 0.46 g of 1f (36% yield, mp 105-106.2 ˚C). Under similar condition, products 1c and 1e were not obtained, but, 1g was appeared in very small amount. IR (KBr) cm^{-1}: 3410 (NH), 2980, 2940, 1616, 1592, 1558, 1264, 952 (N-O). M/z, 157 $(M+1)^+$, 156 (M^+).

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