Microwave mediated fast synthesis of diaminoglyoxime and 3,4-diaminofurazan: key synthons for the synthesis of high energy density materials

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This paper reports the first microwave-assisted synthesis of diaminoglyoxime (DAG) and diaminofurazan (DAF). The synthesis involved the vicarious nucleophilic substitution of H of glyoxime using hydroxylamine hydrochloride under microwave irradiation for 2 to 3 min to obtain DAG, which on further irradiation in alkali solution for 20 min yielded DAF. Conversion of glyoxime into DAF was also achieved in a one pot sequence in good overall yield using microwave irradiation.

Keywords: diaminoglyoxime, diaminofurazan, microwave irradiation

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Owing to increased perception of threat with the introduction of long-range projectiles and missiles, including intercontinental ballistic missiles (ICBM), there is a continued demand for insensitive high explosives (IHEs). The unprecedented quest for novel high energy materials (HEMs) with low vulnerability and highest possible performance has led to the discovery of insensitive power packed materials[1-3] such as 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), 3-nitro-1,2,4-triazole-5-one (NTO), 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclododecane (TEX), 1,1-diamino-2,2-dinitroethene (FOX-7) and 2,6-diamino-3,4-dinitropyrazine oxide (LLM-105). Many of these insensitive HEMs are at various stages of their pilot plant production in different countries.

The furazan ring[4,5] itself has been used as an energetic moiety. It has been demonstrated that even the simplest substituted furazans free of the other energetic groups possess the increased energy and can under certain conditions results in quick (at burning) or instantaneous (at explosion) energy release. DAF is not exceptional in this regard. More recently, a variety of newly synthesised nitroamino furazans have been reported to have high-energy potential. [6,7] DAF is an important intermediate for the synthesis[8,9] of high density liquid and solid energetic materials, zero hydrogen compounds, high energy fuels, oxidants and thermally stable HEMs. Theoretical modelling studies reported by Russian workers[10] bring out the potential of furazan and furoxans obtained from DAF (precursor) as advanced HEMs. DAF is also reported[11,12] to be used as a burn rate suppressant for composite propellants.

The synthesis of DAF was initially accomplished in Russian research laboratories[11] by multi-step procedures. However, these approaches resulted in low as well as capricious yields and problems associated with the isolation of intermediates was another cause of concern. In one of the methods[11] reported for the synthesis of DAF, vicarious nucleophilic substitution (VNS) reaction was used. In view of the prime importance of DAF in the area of synthesis of advanced HEMs, efforts are being made all over the globe to improve upon the current method of synthesis of DAF, which invariably involves the use of high pressure (28–30 bar) and high temperature (170–180 °C) reactions. Although a few approaches have been reported,[6,11] none of these methods discloses the actual process of the synthesis of DAF.

High-speed microwave synthesis has attracted a considerable amount of attention in recent years.[13] A large number of review articles[14,15] and several books[16,17] provide extensive coverage of the subject.

In view of the prime importance of DAF as a precursor for the synthesis of high-density high-energy materials (HEDMS) and continued interest in the utilisation of microwave chemistry in organic synthesis, we report here the preliminary results obtained in the microwave-assisted fast synthesis of DAG and DAF. The synthesised compounds have been characterised by spectral and thermal methods.

Results and discussion

The vicarious nucleophilic substitution (VNS) reaction of glyoxime with hydroxylamine hydrochloride offers a cleaner high yielding method of preparation of DAG in comparison to the conventional method[6] involving preparation of dithioxamide as reactant but this conversion requires 5–6 h at 90 °C. The use of microwave mediation (M.W.) helps to reduce the reaction time (6 h to 3 min) drastically with good yields. The conversion of DAG to DAF also has been achieved under microwave conditions as shown in Scheme 1. This method is of great importance in view of the ease of synthesis of DAF as the conventional method[6] of its synthesis involves high pressure and temperature conditions.

During microwave-assisted synthesis of DAG and DAF a series of experiments were conducted by changing the reaction conditions. The power used was varied from 150 to 800 W and the reaction conditions were standardised by varying the time from 30 s to the time voted to obtain the product. The power, time and yield used for each of the above compounds are listed in Table 1.

Table 1 Microwave assisted synthesis of DAG and DAF

Reaction	Time/min.	Power/Ws	Yield/%
Glyoxime to DAG	2–3	300	60
DAG to DAF	20	800	70 (42 % overall from glyoxime)
Glyoxime to DAF	2–3	300	
	30	800	70

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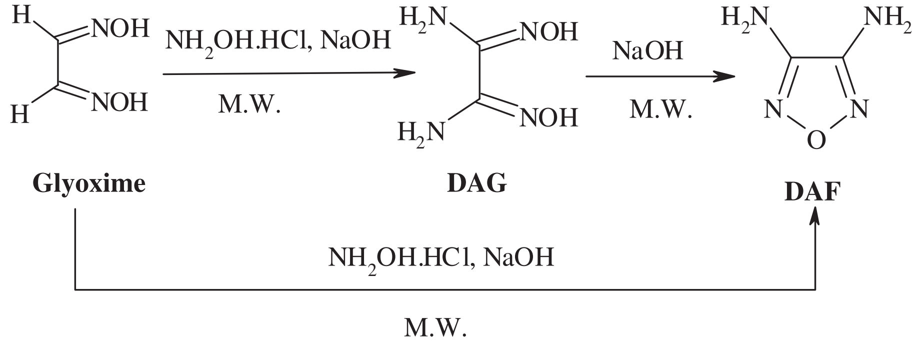

Scheme 1

Subsequently DAF was prepared in a one-pot reaction sequence from glyoxime using microwave irradiation without isolating DAG. In this reaction the synthesis of DAF was achieved in 30 min at the power of 800 W (after the initial 2–3 min at 300 W followed by allowing the reation to subside) in 70 % overall yield. The one-pot reaction sequence was shown to be the best method for the synthesis of DAF.

The formation of DAG and DAF was confirmed by IR, NMR and mass spectral data, which were consistent with the reported[6] values. DSC of DAG exhibited an endotherm in the temperature range of 201–203 °C, which is close to the reported[6] melting point. The absence of an –OH stretching frequency (3470 cm^{-1}) and the presence of an N–O–N stretching frequency (1050–1150 cm^{-1}) in the IR spectrum of DAF indicated the conversion of DAG into DAF. ^{1}H NMR, ^{13}C NMR, and mass spectral data also confirmed the formation of DAF. The DSC of DAF showed an endotherm with peak maximum of 182 °C, which is also in close agreement with the reported[6] melting point of DAF.

Conclusion

A microwave mediated fast synthesis of DAG and DAF has been established during this work. The synthesised compounds have been characterised by spectroscopic and thermal techniques. The spectroscopic results obtained are in agreement with the reported data. The thermal decomposition pattern in DSC matches with the reported data for DAG and DAF.

Experimental

All the reagents and chemicals used in the present study were of AR grade and used as such without further purification. The IR spectra were recorded on Perkin Elmer FTIR-1600 spectrophotometer in a KBr matrix. The ^{1}H NMR spectra were determined on a 300 MHz Varian instrument in a mixture of deuterated chloroform and DMSO with TMS as an internal standard. Mass spectra of the samples were recorded by the electron impact method (70 eV) using a Finnigan Mat instrument (Model 1020). The microwave oven used was a Daewoo Model No. KOR 616 T (150 to 800 watt).

Caution: General laboratory safety precautions should be followed during the synthesis of diamino furazan (DAF). A safety fume hood should be used for all the reactions carried out using a microwave oven.

Microwave-assisted synthesis of DAG: Aqueous sodium hydroxide solution (100 ml, 5 M) was added to glyoxime (17.6 g, 0.02 mol) and contents were kept under stirring. Subsequently, hydroxylamine hydrochloride (27.8 g, 0.04 mol) was added and the contents were irradiated in the microwave oven at the power of 300 W for 2–3 min. During this period, a break of 30 s was given when the reaction mixture started boiling. The flask was taken out of the microwave oven after 3 min when a vigorous reaction started. The reaction was allowed to subside at room temperature. The mixture was cooled in ice and colourless needles were isolated after filtration. The crystals were washed with cold water and dried to give DAG. (14.5g, 60 %). M.p. 201–202 °C Lit[6] m.p.203 °C IR (KBr) 3470 (–OH), 3368, 3104 (–NH_2), 1654 (C=N), ^{1}H NMR (DMSO d^6) δ 5.2 (s, 4H, NH_2), 9.8 (s, 2H, OH). MS : 118 (*m/z* and base peak)

Microwave-mediated synthesis of DAF: An aqueous solution of potassium hydroxide (40 ml, 2 M) containing DAG (11.8 g, 0.1 mol) was placed in a glass reaction vessel and irradiated in the microwave oven for 20 min with a break of 30 s, whenever required to avoid evaporation of water and to keep the reaction in the aqueous medium using power of 800 W. The contents of the reaction mixture were allowed to cool in ice and the product obtained was washed with cold water to furnish DAF (7.2g, 70 % and 42 % overall yield from glyoxime); m.p. 180–181°C, Lit.[6] m.p. 178–80 °C. IR (KBr): 3423, 3318 (NH_2), 1647 (C=N), cm^{-1}. ^{1}H NMR (DMSO d^6) δ 5.81 (bs, 4 H, NH_2), MS: *m/z*: 100, (base peak).

One pot synthesis of DAF from glyoxime: An aqueous solution of sodium hydroxide (100 ml 7.5 M) was added to glyoxime (17.6 g, 0.2 mol) and mixture was kept under stirring. Subsequently, hydroxylamine hydrochloride (27.8 g, 0.4 mol) was added, and the contents were irradiated in the microwave oven at the power of 300 W for 2–3 min. During this period, a break of 30 s was given when the reaction mixture started boiling. The flask was taken out of the microwave oven after 3 min when the vigorous reaction started. The reaction was allowed to subside at room temperature. The reaction mixture was further irradiated in microwave oven for 30 min with a break of 30 s, whenever required (see above), using a power of 800 W and was cooled to get a solid product. After washing with water, DAF (14g, 70 %) was isolated.

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References

1 V.T. Ramakrishnan, M. Vedachalam and J.H. Boyer, *Heterocycles*, 1990, **31**, 479.

2 P. Lamy, C.O. Leiber, A.S. Cumming and M. Zimmer, Air Senior National Representatives long term technology project on insensitive high explosives (IIEs): Studies of high energy insensitive high explosives. Proc., 27th *International Annual Conference of ICT*, Karlsrushe, Federal Republic of Germany, 1996, 1-1 – 1-14.

3 B.M. Dobratz, M. Finger, L.G. Green, J.R. Humphrey, R.R. McGuire and H.F. Rizzo, *The Sensitivity of Triaminotrinitrobenzene (TATB) and TATB Formulations: Summary and Report*, Lawrence Livermore National Laboratory, Livermore, CA, UCID-17808, 1978.

4 R.L. Willer, M.S. Chi, R Gleeson and J.C. Hill, US Patent 5071495.

5 V.G. Andrianov and A.V. Eremeev, *Khim. Geterotsikl. Soedin.*, 1984, 1155.

6 A. Gunasekaran, M. Trudel and J.H. Boyer, *Heteroat. Chem.*, 1994, **5**, 441.

7 V.O. Kulagina, T.S. Novikova and L.I. Khmelnitskii, *Chem. Heterocycl. Compd*., 1994, **30**, 629.

8 G.D. Solodyuk, M.D. Boldyrev, B.V. Gidaspov and V.D. Nikolaev, *Zh. Org. Khim*. 1981, **17**, 861.

9 A.B. Sheremetev and N.S. Aleksandrova, *Mendeleev Commun.*, 1998**, 6**, 238.

10 T.S. Pivina, V.S.Alekei, V. Evtushenko and L.I. Khemelnitskii, *Propellants, Explos., Pyrotech.*, 1995, **20**, 5.

11 A.K. Zelenin and M.L. Trudell, *J. Heterocycl. Chem.*, 1997, **34**, 1057.

12 M.A. Hiskey, N. Goldman and J.R. Stine, *J. Energ. Mater.*, 1998, **16**, 119.

13 D. Adam, *Nature* 2003, **421**, 571.

14 S. Caddick, *Tetrahedron*, 1995, **51**, 10403.

15 P. Lidstrom, J. Tierney, B. Wathey, and J. Westman, *Tetrahedron*, 2001, **57**, 9225.

16 A. Loupy, *Microwaves in Orginic Synthesis*, 1st Edn. Wiley-VCH, 2002.

17 B.L. Hayes, *Microwave synthesis: Chemstry at the Speed of Light*, 1st Edn. CEM, 2002.