

Microwave-Assisted Quick Synthesis of Some Potential High Explosives

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Abstract: This paper reports a novel microwave-assisted method for the synthesis of potential high explosives (HEs) such as 3-nitro-1,2,4-triazol-5-one (NTO), bis-(2,2-dinitropropyl) nitramine (BDNPN), 4-nitroimidazole (4-NI) and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20). The high temperature thermal rearrangement of

1,4-dinitroimidazole to 2,4-dinitroimidazole was also reported using microwave radiation as heating source. The synthesized compounds were characterized by spectroscopic techniques and the data obtained confirmed their structures.

Keywords: High explosives · Microwave · Quick synthesis: Thermal rearrangement

1 Introduction

In recent decades, many significant advances in organic chemistry, such as novel synthetic reagents and methods, as well as the advent of an array of analytical techniques, have improved the dynamic and effectiveness of organic chemistry. However, the practical aspects for carrying out laboratory-scale reactions have changed little during this period. Especially when heating is necessary, mainly oil baths and heating jackets are used. These traditional heating techniques are slow and time-consuming, and sometimes can lead to overheating and decomposition of the substrate and product. Microwave (MW) irradiation, an unconventional energy source, is an effective alternative to conventional heating since it utilizes the ability of liquids or solids to transform electromagnetic energy into heat energy. The microwave irradiation has been applied to a number of processes such as organic synthesis, polymer technology, pharmaceutical, waste treatment, ceramic/alkane decomposition etc. Microwave assisted chemical synthesis have stimulated considerable attention in the recent years [1–19]. Microwave heating is very useful in organic synthesis in many dimensions; reactions can be performed effectively and efficiently with high reaction rates [20–23]; it causes few by-products coupled with high yields and experimental simplicities. Microwave reactors provide a clean and cheap alternative to conventional oil bath and heating mantles. Further, these reactions can be run at atmospheric pressure in reflux systems. In view of these advantages, more focus has been devoted in this decade to microwave-enhanced chemical reactions. Nevertheless, the utilization of microwave irradiation for the preparation of explosives is seldom, which may be due to the hazards associated in it. Microwave-induced chemical synthesis of energetic materials is seldomly reported and only few information is available [24,25].

This paper reports a novel microwave-assisted quick method for the synthesis of potential high explosives such as 3-nitro-1,2,4-triazol-5-one (NTO), bis-(2,2-dinitropropyl)-nitramine (BDNPN), 4-nitroimidazole (4-NI), and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20). Another important high explosive, 2,4-dinitroimidazole, was also prepared from 1,4-dinitroimidazole by thermal rearrangement using microwave radiation [26].

2 Experimental Section

2.1 Materials and Methods

All the reagents and chemicals used in the present study were of AR grade and used as such. The microwave reactions were carried out by irradiating the reaction mixture using a microwave reactor (RAGA'S) with a power of 700 W coupled with a reflux system, temperature digital display, temperature IR sensor and magnetic stirring. The IR spectra were recorded with a Nicolet FTIR-5700 spectrophotometer in KBr matrix. ¹H NMR spectra were recorded with a 300 MHz Varian instrument at 30 °C with TMS as an internal standard. DSC studies were undertaken with a Perkin-Elmer DSC-7 instrument operating at heating rate 10 Kmin⁻¹ in nitrogen atmosphere with 1 mg of sample.

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Table 1. Reaction conditions for the preparation of HEs using microwave radiation.

Sl. No.	Substrate	Reagent used		Duration /min	Temp. /°C	Product obtained	Yield /%
		Quantity	Quantity				
1	Triazolone (TO)	0.5 g (0.0059 mol)	HNO ₃ (70%) 5 mL	10	65	NTO	74 ^{a)}
2	2,4,8,12-Tetraacetyl- 2,4,6,8,10,12- hexaazaisowurtzitane (TAIW)	0.5 g (0.0015 mol)	HNO ₃ (98%) 4 mL H ₂ SO ₄ (98%) 1 mL	5	75	CL-20	94
3	Imidazole	1.5 g (0.022 mol)	HNO ₃ (70%) 3.1 mL H ₂ SO ₄ (98%) 3.1 mL	15	120	4-NI	55
4	Bis-(2,2- dinitropropyl)-amine (BDNPA)	1 g (0.0036 mol)	HNO ₃ (98%) 4 mL	15	65	BDNPN	85
5	1,4-Dinitroimidazole (1,4-DNI)	0.5 g (0.0032 mol)	Chlorobenzene 5 mL	20	125	2,4-DNI	90

a) In the process of washing, some amount of NTO gets dissolved. Hence the yield is lowered.

2.2 General Procedure for Synthesis Using Microwave Irradiation

All reactants were used as given in Table 1.

Caution! We never experienced any explosion in any of our experiments during microwave heating. However, proper care was taken while carrying out these reactions.

2.2.1 Nitration

In a flat bottom reaction vessel nitric acid was cooled to 10 °C using an ice bath. Calculated amount of H₂SO₄ was added wherever required and the solid precursor was added portion wise whilst stirring keeping the temperature below 15 °C. The reaction assembly was fixed in a microwave reactor with a condenser and exposed to microwave radiation at 30% power level (210 W) for about 5–15 min (varies with respect to the reaction), the temperature was raised up to the temperature given in Table 1. After completion of the reaction (monitored by using silica gel TLC technique), the reaction mixture was allowed to cool to ambient temperature and quenched over crushed ice. The solid precipitate was collected by filtration and washed with little amount of ice cooled water. The product was dried in a water-jacketed oven at 50 °C. Experimental conditions, compounds, and yields are listed in Table 1. The characterization data of the products are summarized in Table 2.

2.2.2 Rearrangement of 1,4-Dinitroimidazole to 2,4-Dinitroimidazole

1,4-Dinitroimidazole (0.5 g, 0.0032 mol) was put in a flat bottom reaction vessel together with chlorobenzene (5 mL). The reaction vessel was fixed in a microwave reactor with a condenser and exposed to microwave radiation at 30% power level (210 W) for about 20 min, the temperature was raised up and kept at 125 °C. After completion of

the reaction (monitored by using silica gel TLC technique), the reaction mixture was allowed to cool to ambient temperature. The solid precipitate was collected by filtration and washed with little amount of hexane. Afterwards, the mother liquor was treated with hexane (10 mL) to recover a second crop of 2,4-DNI. The product was dried in a water-jacketed oven at 50 °C. The characterization data of the products are summarized in Table 2.

3 Results and Discussions

The synthesized compounds were characterized by spectroscopic and thermal techniques. The results reveals that the characterization data of NTO, CL-20, 4-NI, 2,4-DNI, and BDNPN match with the reported results [27–30].

Microwave irradiation enhances the rate of reaction of nitration of triazolone (TO) to 3-nitro-1,2,4-triazol-5-one (NTO), 2,4,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane (TAIW) to 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20), bis-(2,2-dinitropropyl)amine (BDNPA) to bis-(2,2-dinitropropyl)nitramine (BDNPN), imidazole to 4-nitroimidazole and thermal rearrangement of 1,4-dinitroimidazole (1,4-DNI) to 2,4-dinitroimidazole (2,4-DNI). It was found that using microwave radiation as a heating source the reaction times were drastically reduced along with a similar yield of the pure products. The experimental results obtained were compared with those obtained by conventional method of preparation with respect to time and yield (Table 3). From Table 3 it is obvious that microwave assisted syntheses of high energy materials process quickly with high yields, which are similar to conventional methods.

In addition to that, in case of conventional heating most of the above reactions evolve huge amount of oxides of nitrogen (NO_x) throughout the reaction period. In this approach, the evolution of NO_x is far less (or in some cases

Table 2. Characterization data of synthesized compounds.

Compounds	IR /cm ⁻¹ (in KBr)	¹ H NMR		DSC, T _{max} /°C
		Chemical shift δ /ppm	Solvent used	
	3196 (–NH), 1689 (–C=O), 1540 and 1336 (–NO ₂)	8.27,(br. s, 2 H, –NH–)	DMSO- <i>d</i> ₆	256 (Exo.)
	3040 and 2844 (–CH <), 1614 and 1332 (–NO ₂)	8.2 (s, 2 H, –CH <), 8.34 (s, 4 H, –CH <)	(CD ₃) ₂ CO	254 (Exo.)
	3448 (–NH–), 3141 and 3010 (–CH=), 1557 and 1332 (–NO ₂)	13.2 (br. s, 1 H, –NH–), 8.3 (s, 1 H, –CH=), 7.8 (s, 1 H, –CH=)	DMSO- <i>d</i> ₆	308 (Endo.)
	2987 (–CH ₂ –), 1580 and 1344 (–NO ₂)	5.2 (s, 4 H, –CH ₂ –), 3.34 (s, 6 H, –CH ₃)	DMSO- <i>d</i> ₆	189 (Exo.)
	3420 (–NH–), 3149 (–CH=), 1554 and 1354 (–NO ₂)	8.3 (br. s, 1 H, –NH–), 10.2 (s, 1 H, –CH=)	DMSO- <i>d</i> ₆	272 (Exo.)

Table 3. Comparison of microwave reaction and conventional method of synthesis of potential HEs.

Compound	Duration of time/min		Yield /%	
	Conventional	Microwave	Conventional	Microwave
NTO	120	10	85	74
CL-20	240	5	90	94
4-NI	360	15	52	55
BDNPN	180	15	80	85
2,4-DNI	240	20	95	90

non-existent) for shorter durations. This is highly advantageous in terms of gaseous hazardous materials mitigation.

4 Conclusions

The present study demonstrates the microwave-assisted synthesis of IHEs such as NTO, BDNPN, CL-20, nitroimidazole, and dinitroimidazole in short reaction times with high yields, which are similar to those of conventional methods. The synthesized compounds were characterized using IR and NMR spectroscopy. The nitration method used in the present study is of particular interest for the high energy

materials researchers, scientists, and technologists in terms of saving time in the synthesis process along with an increase in yield and purity of the products. The microwave technique seems to be a useful approach for the synthesis of various promising explosives.

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