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Contributed Paper

Rapid and Efficient Synthesis of 4-[(tri fluorine methyl)-2, 6-di Nitro Phenyl Amino]-4, 3-di hydro-6-methyl-3-thioxo-1, 2, 4-Triazine-5-ones Derivatives by Nano MgO under Microwave Irradiation

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ABSTRACT

In this research work, 4-[(tri fluorine methyl)-2,6-di nitro phenyl amino]-4,3-di hydro-6-methyl-3-thioxo-1,2,4-Triazine-5-one was produced from the reaction between 2-chloro-1,3-di nitro-5-triflouro methyl benzene and 4-amino-6-methyl-5-one-3-thion-1,2,4-Triazine through two methods (1-reflux & 2-microwave) in the presence of suitable solvents Using Nano catalyst MgO under microwave conditions have been reported. The MAOS method is more effective in synthesizing these compounds than the conventional method regarding to the higher chemical yields of products (54% to 96%) and the shorter reaction times (7 to 10 minutes). Structural, optical and nanostructures by X-ray diffraction X (XRD), scanning electron microscopy (SEM). The 1H-NMR and other methods like FT-IR and Mass spectroscopy have determined all of the compounds. Obtained results of synthesized compounds showed that reactions were carried out with suitable speed and range of products, low response time, high catalytic activity, and excellent products and environmentally friendly the results of this protocol are very important.

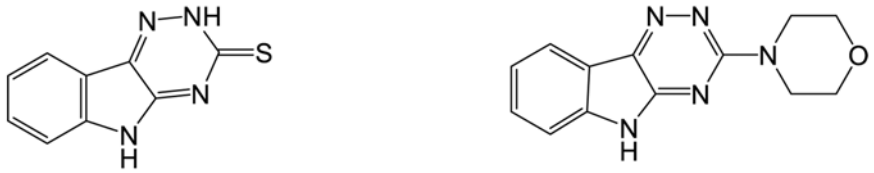
Keywords: microwave assisted organic synthesis, conventional method, ^{1}H NMR, 1, 2, 4-triazine, 2-chloro-1, 3-di nitro-5-triflouro methyl benzene, nano MgO

1. INTRODUCTION

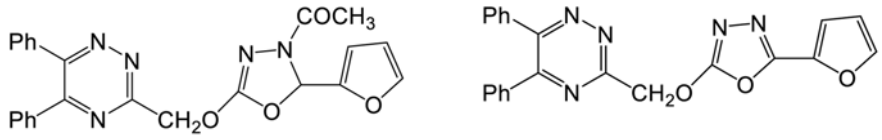
1,2,4-Triazines and their derivatives have been widely studied in terms of their synthetic methodologies and reactivity since some of these derivatives were reported to have promising biological activities [1, 2]. Triazine Herbicides are mainly in the soil. They are widely used to control broadleaf weeds and grasses used for one year. Some of the triazine oil can be used on shoots and leaves of plants, Of course they are important exceptions Symazine, propazines and limited activity on foliage plants with

soil [3]. Triazine derivatives are of great importance because they exhibit significant biological and pharmacological activities including Anti-microbial, anti-viral, Herbicides strong and anti-inflammatory [4, 5]. These compounds are also used as antihypertensive drugs have been tried on mice, and guinea pigs retardancy properties thrombocytes in the blood have been shown (Scheme 1) [6].

A series of 5, 6-diphenyl-1, 2, 4-Triazine also has anti-microbial, anti-viral and anti-inflammatory respectively. Anti-inflammatory properties of these compounds was studied [7].



Scheme 1. Examples of triazine drugs (antihypertensive).



Scheme 2. Examples of triazine drugs (anti-inflammatory).

The main building consists of carbon atoms and nitrogen molecules Triazine ring (nitrogen heterocyclic building). Are symmetrical Triazine such that the carbon and nitrogen atoms are in the ring alternately. Although the ring is asymmetrically metribuzin. Depending on the location of the R1 substituent in the ring, Triazine divided into three main groups:

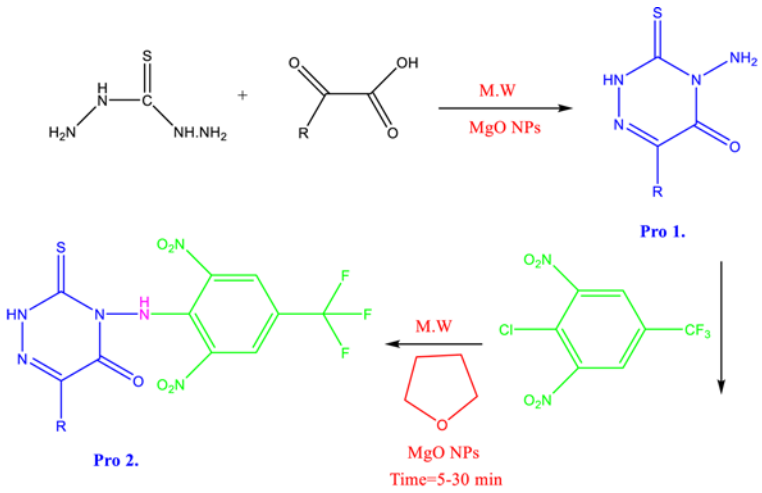
1. Chloro Triazine chlorinated and their public name (zine) ends like Symazine, atrazine, Syanazine and propazines.

2. Operating replaced methyl tio Triazine factor in the methyl group is SCH_3 and general name of the (trine) ends like Ametrine, Torbotrine and Promtrine.

3. Methoxy Triazine, such as Prometine mobility and durability in comparison to the other two groups, but have less choice [8-11].

The synthesis of 1, 2, 4-Triazines and their derivatives are well documented and their methods of preparation are manifold and varied. There are several methods for the synthesis of Triazine from thio ones, reaction of Acyl nitrile with aminoguanidin, reaction phenyl phetalazine with aminoguanidin, Alpha di carbonyl with salicylic hydrazide and Ammonium acetate in glacial acetic acid. However, some of these methods suffer from disadvantages such as long reaction times, low yields, difficulty in preparation of starting materials and tedious workup [12]. Heating reactions with traditional equipment, such as oil baths, sand baths and heating mantles, is not only slow, it creates a hot surface on the reaction vessel where products, substrates and reagents often decompose over time [13]. The application of microwave irradiation in reactions is a promising technique [14]. The aim of this work is to synthesize some 4-[(tri fluorine methyl)-2, 6-di nitro phenyl amino]-4, 3-di hydro-6-methyl-3-thioxo-1, 2, 4-Triazine-

5-ones derivatives via the novel method in an organic system under microwave irradiation by Nano MgO catalyst. This study describes a successful a roach for the synthesis of 4-[(tri fluorine methyl)-2, 6-di nitro phenyl amino]-4, 3-di hydro-6-methyl-3-thioxo-1, 2, 4-Triazine-5-ones in a domestic microwave oven. This microwave technology does not require linking-cleaving chemistry but afford the products immediately. Microwave-assisted organic synthesis is beginning to play a greater role in process development, especially in cases where classical methods require prolonged reaction times and forced conditions. It is included from the results of this study that the Microwave Assisted Organic Synthesis (MAOS) method by Nano MgO catalyst results in higher chemical yields of the products with shorter reaction time than the conventional (reflux) method (Scheme 3).



Scheme 3. Synthetic route for the 4-[(tri fluorine methyl)-2, 6-di nitro phenyl amino]-4, 3-di hydro-6-methyl-3-thioxo-1, 2, 4-Triazine-5-ones by Nano MgO under microwave conditions.

2. MATERIALS AND METHODS

2.1 General Method

All the reactions that were carried out using a melting point were determined on a Gllenkamp FB.600-olof, all melting points are uncorrected and were determined in capillary tube on Boetius melting point microscope. All of the reagents used in this research are GR grade. Melting points were taken in open capillaries and are uncorrected. IR spectra were recorded on Perkin-Elmer-1420 spectrophotometer. 1HNMR spectra (DMSO) were recorded on Gemini-200 MHz spectrophotometer with TMS as internal standard.

2.2 Synthesis of Magnesium Oxide Nanoparticles

A solution of 1 mol/L sodium hydroxide was added drop-wise to a solution prepared from dissolving 2 g of Mg $(NO_3)_2.6H_2O$ and 0.5 g polyvinyl pyrolydon (PVP) as surfactant. Then the reaction mixture was sonicated for 30 min ultrasonic power 90 W. The prepared gel was centrifuged and washed several times with deionized water and ethanol, and finally calcined in a furnace at 600 °C for 2 h.

2.3. General Procedure for the Synthesis of 4-((2, 6-dinitro-4-(trifluoromethyl) phenyl) amino)-6-ethyl-3-thioxo-3, 4-dihydro-1, 2, 4-Triazine-5(2H)-one derivatives Compounds.

A. Conventional method

In the amount of 0.1 g 4-amino-6-ethyl-5-one-3-thion-1, 2, 4-Triazine in 2 ml of ethanol dissolved and poured into the flask with two openings and mixed with cooling in a water bath to 60 °C was placed. After 30 minutes, the 0.17 gr of 2-chloro-1, 3-dinitro-5-(trifluoromethyl) benzene added and after 20 minutes the amount of 3 ml of pyridine was added to the flask and the reflux for 3 hours. The progress of the reaction was monitored by TLC (eluent: EtOAc/MeOH, 4:1). After completion of the reaction, the mixture was cooled to room temperature. The solvent was evaporated and the crude product was recrystallized to afford the pure product in 91% yields (Table 1).

B. Microwave method

A mixture of 4-amino-6-ethyl-5-one-3-thion-1, 2, 4-Triazine (0.1 gr) in the solvent tetrahydrofuran, 2-chloro-1,3-dinitro-5-(trifluoromethyl)benzene (0.17 gr), pyridine (2 ml) and Nano MgO (3 mol %) is ground thoroughly and irradiated in a microwave oven at 180 W for about 360 sec at an interval of 30 seconds. During the irradiation, the solid melts and a sticky crude product is formed upon cooling. It is further purified by column chromatography to give the pure products in good to excellent yield. All the products were characterized by melting point, NMR, IR, mass spectra and CHN analysis.

2.3.1 Spectral data

Hydrazinecarbothiohydrazide (I):

Two openings within a balloon with 150 ml of distilled water and 50 ml of hydrazine hydrate refrigerant poured into the flask in an oil bath to a temperature of fifty degrees Celsius and then, carbon disulfide is added slowly over a period of one hour. After the carbon disulfide and then for an hour to an hour and a half temperature to 150 to 140 °C and then we have to act reflux to well done, then the balloon into an ice bath and then placed overnight, then the solid collected by Buchner funnel and distilled water is crystallization.

To give (0.93 g, 97%); A Orange crystal; Mp: 170- 173 °C; IR (KBr): 3305 (NH_2), 3273 (NH_2), 3205 (NH), 1642 (C=S), 1286 (C-N); ^{1}H NMR (400 MHz, DMSO) δ 3.21 (s, 4H, NH_2), 9.6 (s, 2H, NH); ^{13}C NMR (DMSO) δ 184.2; MS m/z 106 (M^+, 95.65); Anal. Calcd for CH_6N_4S: C, 11.32; H, 5.70; N, 52.78. Found: C, 11.30; H, 5.69; N, 52.73.

4-amino-6-methyl-3-thioxo-3, 4-dihydro-1, 2, 4-Triazine-5(2H)-one (AMTTO) (II).

The amount of 1 g of thiocarbohydrazide with a 2.20 g 2-oxopropanoic acid and Nano MgO (3 mol %) composition in a 50 ml balloon mixed and the reaction mixture in the microwave for 20 minutes and 90 W of power as well. The reaction product in hot distilled water is crystallization.

To give (0.53 g, 92%); A Yellow needle-shaped crystals; Mp: 182- 184 °C; IR (KBr): 3295 (NH_2), 3200 (NH), 1662 (C=O), 1380 (CH_3), 1128 (C=S); ^{1}H NMR (400 MHz, DMSO) δ 2.1 (s, 3H, CH_3), 6.43 (s, 2H, NH_2), 13.8 (J =2 and 8 Hz, s, 1H, NH); ^{13}C NMR (DMSO) δ 16.6, 74.9, 146.00, 158.2; MS m/z 158 (M^+, 85.23); Anal. Calcd for $C_4H_6N_4OS$: C, 30.37; H, 3.82; N, 35.42. Found: C, 30.33; H, 3.81; N, 35.39.

4-amino-6-ethyl-3-thioxo-3, 4-dihydro-1, 2, 4-Triazine-5(2H)-one (III).

To give (0.65 g, 92%); A Yellow needle-shaped crystals; Mp: 140-145 °C; IR (KBr): 3273 (NH_2), 3200 (NH), 1691 (C=O), 1396 (-CH_2-CH_3), 1140 (C=S); ^{1}H NMR (400 MHz, DMSO) δ 1.00 (s, 3H, CH_3), 2.50-2.59 (*J* =2 and 8 Hz, d, 2H, CH_2), 6.47 (s, 2H, NH_2), 8.69 (J =2 and 8 Hz, s, 1H, NH); ^{13} C NMR (DMSO) δ 11.3, 23.8, 146.00, 159.7, 182.1; MS m/z 172 (M^+, 76.50); Anal. Calcd for $C_5H_8N_4OS$: C, 34.87; H, 4.68; N, 32.54. Found: C, 34.85; H, 4.70; N, 32.51.

4-amino-6-(methoxymethyl)-3-thioxo-3, 4-dihydro-1, 2, 4-Triazine-5(2H)-one (IV).

To give (0.85 g, 76%); A pale yellow needles; Mp: 193-195 °C; IR (KBr): 3285 (NH_2), 3210 (NH), 1685 (C=O), 1135 (C=S), 1120 (-CH_2-OCH_3); ^{1}H NMR (400 MHz, DMSO) δ 3.31 (s, 3H, CH_3), 4.21-4.23 (J =2 and 8 Hz, d, 2H, CH_2), 6.26 (s, 2H, NH_2), 13.29 (J =2 and 8 Hz, s, 1H, NH); ^{13} C NMR (DMSO) δ 57.5, 68.6, 147.45, 159.3, 180.16; MS m/z 188 (M^+, 90.10); Anal. Calcd for $C_5H_8N_4O_2S$: C, 31.91; H, 4.28; N, 29.77. Found: C, 31.90; H, 4.27; N, 29.73.

4-amino-6-phenyl-3-thioxo-3, 4-dihydro-1, 2, 4-Triazine-5(2H)-one (V).

To give (0.85 g, 56%); A Brown needle-shaped crystals; Mp: 121-124 °C; IR (KBr): 3290 (NH_2), 3203 (NH), 1662 (C=O), 1580 (C=C stretch, aromatic), 1135 (C=S); ^{1}H NMR (400 MHz, DMSO) δ 6.30 (s, 2H, NH2), 7.56 (s, 3H, CH), 7-96-7.98 (J =2 and 8 Hz, s, 2H, CH), 13.43 (J =2 and 8 Hz, s, 1H, NH); ^{13} C NMR (DMSO) δ 128.8, 128.9, 129.2, 129.4, 131.00, 133.1, 146.4, 159.7, 182.3; MS m/z 220 (M^+, 95.17); Anal. Calcd for $C_9H_8N_4OS$: C, 49.08; H, 3.66; N, 25.44. Found: C, 49.7; H, 3.67; N, 25.42.

4-amino-3-thioxo-6-(p-tolyl)-3,4-dihydro-1, 2, 4-Triazine-5(2H)-one (VI).

To give (0.66 g, 75%); A yellow needles; Mp: 142-144 °C; IR (KBr): 3279 (NH_2), 3210 (NH), 1680 (C=O), 1600 (C=C stretch, aromatic), 1138 (C=S), 750 (C-H, aromatic); ^{1}H NMR (400 MHz, DMSO) δ 2.41 (s, 3H, CH3), 6.26 (s, 2H, NH2), 7.27-7.29 (J =2 and 8 Hz, d, 2H, CH), 7.76 (d, 2H, CH), 13.29 (J =2 and 8 Hz, s, 1H, NH); ^{13} C NMR (DMSO) δ 21.3, 128.9, 129.1, 129.3, 129.4, 130.1, 146.5, 159.3, 182.1; MS m/z 234 (M^+, 65.58); Anal. Calcd for $C_{10}H_{10}N_4OS$: C, 51.27; H, 4.30; N, 23.92. Found: C, 51.28; H, 4.29; N, 23.90.

4-amino-6-(4-ethylphenyl)-3-thioxo-3, 4-dihydro-1, 2, 4-Triazine-5(2H)-one (VII).

To give (0.79 g, 81%); A Pink needles; Mp: 193-195 °C; IR (KBr): 3280 (NH_2), 3210 (NH), 1700 (C=O), 1475 (C=C stretch, aromatic), 1140 (C=S), 750 (C-H, aromatic); ^{1}H NMR (400 MHz, DMSO) δ 1.18 (t, 3H, CH_3), 2.72 (dd, 2H, CH_2), 6.26 (s, 2H, NH_2), 7.31-7.33 (J =2 and 8 Hz, d, 2H, CH), 7.81 (d, 2H, CH), 13.23 (J =2 and 8 Hz, s, 1H, NH); ^{13} C NMR (DMSO) δ 14.5, 28.2, 127.7, 127.8, 129.00, 129.1, 130.3, 146.4, 146.6, 159.7, 179.9; MS m/z 248 (M^+, 82.13); Anal. Calcd for $C_{11}H_{12}N_4OS$: C, 53.21; H, 4.87; N, 22.56. Found: C, 53.20; H, 4.84; N, 22.54.

4-amino-6-(4-ethoxyphenyl)-3-thioxo-3, 4-dihydro-1, 2, 4-Triazine-5(2H)-one (VIII).

To give (0.45 g, 54%); A Yellow needles; Mp: 198-200 °C; IR (KBr): 3295 (NH_2), 3215 (NH), 1695 (C=O), 1600 (C=C stretch, aromatic), 1250 (C-O stretch), 1142 (C=S), 780 (C-H, aromatic); ^{1}H NMR (400 MHz, DMSO) δ 1.34 (t, 3H, CH_3), 4.05 (dd, 2H,

CH_2), 6.29 (s, 2H, NH_2), 7.05-7.07 (J =2 and 8 Hz, d, 2H, CH), 7.80 (d, 2H, CH), 13.31 (J =2 and 8 Hz, s, 1H, NH); ^{13} C NMR (DMSO) δ 14.8, 64.6, 114.5, 114.6, 1247, 129.7, 129.9, 146.4, 159.7, 161.8, 182.1; MS m/z 264 (M^+, 45.43); Anal. Calcd for $C_{11}H_{12}N_4O_2S$: C, 49.99; H, 4.58; N, 21.20. Found: C, 49.50; H, 4.55; N, 21.22.

4-amino-6-(4-hydroxyphenyl)-3-thioxo-3, 4-dihydro-1, 2, 4-Triazine-5(2H)-one (IX).

To give (0.82 g, 91%); A White needles; Mp: 226-228 °C; IR (KBr): 3350 (NH_2), 3300 (OH), 3210 (NH), 1680 (C=O), 1560 (C=C stretch, aromatic), 1000 (C-O stretch), 1140 (C=S), 740 (C-H, aromatic); ^{1}H NMR (400 MHz, DMSO) δ 6.26 (s, 2H, NH_2), 6.82 (d, 2H, CH), 7.64-7.66 (J =2 and 8 Hz, d, 2H, CH), 9.68 (s, 1H, OH), 13.28 (J =2 and 8 Hz, s, 1H, NH); ^{13} C NMR (DMSO) δ 116.00, 116.1, 125.7, 130.6, 130.7, 146.4, 159.7, 160.8, 182.1; MS m/z 236 (M^+, 95.43); Anal. Calcd for $C_9H_8N_4O_2S$: C, 45.76; H, 3.41; N, 23.72. Found: C, 45.75; H, 3.42; N, 23.69.

4-amino-6-(4-chlorophenyl)-3-thioxo-3, 4-dihydro-1, 2, 4-Triazine-5(2H)-one (X).

To give (0.55 g, 77%); A light orange needles; Mp: 235-237 °C; IR (KBr): 3280 (NH_2), 3200 (NH), 1690 (C=O), 1580 (C=C stretch, aromatic), 1138 (C=S), 743 (C-H, aromatic); ^{1}H NMR (400 MHz, DMSO) δ 6.28 (s, 2H, NH_2), 7.51 (J =2 and 8 Hz, d, 2H, CH), 7.75 (d, 1H, CH), 13.29 (J =2 and 8 Hz, s, 1H, NH); ^{13} C NMR (DMSO) δ 128.7, 128.9, 130.5, 130.6, 131.2, 136.6, 146.4, 159.7, 182.3; MS m/z 254 (M^+, 55.13); Anal. Calcd for $C_9H_7ClN_4OS$: C, 42.44; H, 2.77; N, 22.02. Found: C, 42.43; H, 2.76; N, 22.01.

4-amino-6-(4-(dimethylamino) phenyl)-3-thioxo-3, 4-dihydro-1, 2, 4-Triazine-5(2H)-one (XI).

To give (0.83 g, 90%); A red needles; Mp: 219-221 °C; IR (KBr): 3292 (NH_2), 3200 (NH), 1683 (C=O), 1560 (C=C stretch, aromatic), 1440 (CH_3, Bend), 1350 (C-N stretch), 1140 (C=S), 743 (C-H, aromatic); ^{1}H NMR (400 MHz, DMSO) δ 3.02 (s, 6H, CH_3), 6.27 (s, 2H, NH_2), 6.78-6.80 (J =2 and 8 Hz, d, 2H, CH), 7.63 (d, 2H, CH), 13.30 (J =2 and 8 Hz, s, 1H, NH); ^{13} C NMR (DMSO) δ 41.3, 41.4, 111.7, 111.9, 122.6, 130.1, 130.3, 146.5, 153.4, 159.7, 182.00; MS m/z 263 (M^+, 95.87); Anal. Calcd for $C_{11}H_{13}N_5OS$: C, 50.18; H, 4.98; N, 26.60. Found: C, 50.20; H, 4.99; N, 26.59.

6-(4-acetylphenyl)-4-amino-3-thioxo-3, 4-dihydro-1, 2, 4-Triazine-5(2H)-one (XII).

To give (0.35 g, 61%); A pale yellow needles; Mp: 153-155 °C; IR (KBr): 3290 (NH_2), 3210 (NH), 1700 (C=O), 1580 (C=C stretch, aromatic), 1300 (CCOC, Bend), 1139 (C=S), 750 (C-H, aromatic); ^{1}H NMR (400 MHz, DMSO) δ 2.50 (s, 3H, CH_3), 6.26 (s, 2H, NH_2), 7.92-7.94 (J =2 and 8 Hz, d, 2H, CH), 8.08 (d, 2H, CH), 13.27 (J =2 and 8 Hz, s, 1H, NH); ^{13} C NMR (DMSO) δ 26.6, 128.5, 128.7, 129.1, 129.2, 137.5, 139.00, 146.2, 159.8, 182.1, 197.00; MS m/z 262 (M^+, 85.13); Anal. Calcd for $C_{11}H_{10}N_4O_2S$: C, 50.37; H, 3.84; N, 21.36. Found: C, 50.35; H, 3.83; N, 21.35.

4-((2,6-dinitro-4-(trifluoromethyl) phenyl) amino)-6-methyl-3-thioxo-3, 4-dihydro-1, 2, 4-Triazine-5(2H)-one (XIII).

At first the amount of 1.0 g of 4-amino-6-methyl-5-one-3-thione-1, 2, 4-Triazine in the test tube and in the solvent tetrahydrofuran

(dimethyl sulfoxide or ethanol) solution, and then 0.175 g 2-chloro-1, 3-dinitro-1-5-tri fluorine methyl benzene added. The Erlenmeyer flask was placed in the microwave oven and irradiated for 5-30 minute in a domestic microwave oven (Samsung) at low power (operating at 360 W, After irradiation, the temperature of the mixture was 45 °C). The reaction mixture was allowed to cool at room temperature. The ethyl acetate was used as a solvent for TLC. It was washed and purified with a mixture of 2 mL of pure water. The product was crystallized from pure ethanol to give the pure product in yields of 76%92%.

To give (0.75 g, 65%); A Orange crystal; Mp: 196-198 °C; IR (KBr): 3281 (NH), 1543 (C=O), 1381 (CH_3), 1137 (C=S); ^{1}H NMR (400 MHz, DMSO) δ 2.1 (s, 1H, CH_3), 8.72-8.74 (J =2 and 8 Hz, d, 2H, Ar-CH), 10.34 (s, 1H, NH), 13.70 (J =2 and 8 Hz, s, 1H, NH, Triazine ring); ^{13} C NMR (DMSO) δ 16.3, 122.1, 123.2, 128.3, 128.6, 135.2, 135.4, 140.1, 146.00, 159.7, 182.1; MS m/z 392 (M^+, 50.64); Anal. Calcd for $C_{11}H_7F_3N_6O_5S$: C, 33.68; H, 1.80; N, 21.42. Found: C, 33.67; H, 1.82; N, 21.41.

4-((2,6-dinitro-4-(trifluoromethyl) phenyl) amino)-6-ethyl-3-thioxo-3, 4-dihydro-1, 2, 4-Triazine-5(2H)-one (XIV).

To give (0.87 g, 96%); A Orange crystal; Mp: 202-204 °C; IR (KBr): 3094 (NH), 1547 (C=O), 1139 (C=S), 1123 (-CH_2-OCH_3); ^{1}H NMR (400 MHz, DMSO) δ 2.1 (s, 1H, CH_3), 3.1 (dd, 2H, CH_2), 8.74 (J =2 and 8 Hz, d, 2H, Ar-CH), 10.35 (s, 1H, NH), 13.29 (J =2 and 8 Hz, s, 1H, NH, Triazine ring); ^{13} C NMR (DMSO) δ 11.3, 23.8, 122.2, 123.00, 128.1, 128.4, 135.2, 135.3, 140.00, 146.10, 159.7, 182.2; MS m/z 392 (M^+, 50.64); Anal. Calcd for $C_{12}H_9F_3N_6O_5S$: C, 35.47; H, 2.23; N, 20.68. Found: C, 35.44; H, 2.25; N, 20.67.

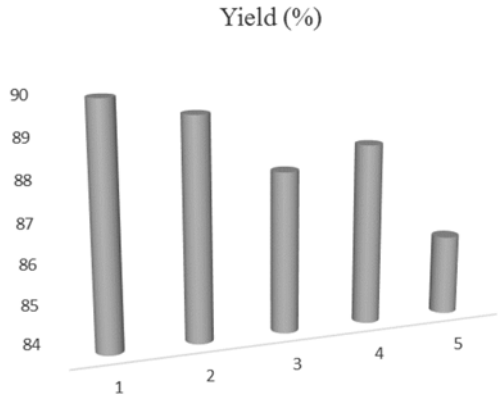
4-((2,6-dinitro-4-(trifluoromethyl) phenyl) amino)-6-(methoxymethyl)-3-thioxo-3, 4-dihydro-1, 2, 4-Triazine-5(2H)-one (XV).

To give (0.59 g, 82%); A White crystal; Mp: 201-203 °C; IR (KBr): 3283 (NH), 1545 (C=O), 1453 (-CH2-CH3), 1135 (C=S); ^{1}H NMR (400 MHz, DMSO) δ 3.31 (s, 1H, CH_3), 4.21 (s, 2H, CH_2), 8.55 (s, 1H, NH), 8.58-8.60 (J =2 and 8 Hz, d, 2H, Ar-CH), 13.31 (J =2 and 8 Hz, s, 1H, NH, Triazine ring); ^{13} C NMR (DMSO) δ 57.5, 68.6, 122.1, 123.2, 128.00, 128.1, 135.4, 135.6, 140.1, 146.00, 159.5, 182.1; MS m/z 422 (M^+, 85.67); Anal. Calcd for $C_{12}H_9F_3N_6O_6S$: C, 34.13; H, 2.15; N, 19.90. Found: C, 34.12; H, 2.13; N, 19.21.

2.4 Recycling Nanoparticles

We also investigated recycling of the MgO NPs as catalyst under ultrasonic irradiation in ethanol (Figure 2). After the completion of the reaction (TLC), $CHCl_3$ was added. The catalyst was insoluble in $CHCl_3$ and it could therefore be recycled by a simple filtration. The nanoparticles were then washed three to four times with methanol and dried at 75 °C for 6 h. The catalyst could be reused for five times with a minimal loss of activity (yields 86 to 90). Perhaps, activity of MgO NPs is decreased by the number of regenerations without any significant loss in catalytic activity (Scheme 4.). When reaction was completed, MgO NPs were collected on the side wall of the reaction vessel with the aid of an external magnet and water was removed from the mixture to leave a residue (including the product and catalyst). Then, the residue was dissolved in ethanol and catalyst was easily separated from the product by attaching an external magnet onto the reaction vessel, followed by decantation of product solution.

Remaining catalyst was washed with ethanol to remove the residual product, dried under vacuum and reused for five subsequent reaction cycles without any significant loss in catalytic activity.



Scheme 4. Recyclability of MgO NPs.

3. RESULT AND DISCUSSION

Researchers have been focused much attention to the one dimensional nanostructure of nanomaterial's for their applications in Nano-electronic devices. MgO is typical wide band gap (7.2eV) semiconductor, represents an important class of functional metal oxides with a broad range of properties [15-17]. The high surface reactivity, high chemical and thermal stability of MgO makes it a promising material for the application in sensors, catalysis, paint and additives etc [15-20].

In order to study the morphology and particle size of MgO nanoparticles, scanning electron microscopy (SEM) image of MgO NPs is presented in figure 1. Clearly shows highly uniform sphere-like structure with rippled-shaped pores. Interestingly, two to three porous spheres are found to be aggregated regularly to form complex structures of NiO. The cause of the aggregation seems to be the effect of calcined, which creates "hot surface" on the initially formed NiO porous spheres. The "hot surfaces" induce mass transport and directional fusion of porous spheres to form arranged superstructures [21-22].

The XRD patterns of functionalized MgO NPs are shown in Figure 2. The diffraction of the MgO Nanoparticles observed in the peaks at 2θ = 37.153, 43.945, 63.595, 75.125 and 79.185 in Figure 2. These data are in good agreement with that of MgO nanoparticles reported before. The crystalline nature of the synthesized MgO NPs sample was further verified by X-ray diffraction pattern (XRD). The crystallite size diameter (D) of the MgO NPs has been calculated by the Debye–Scherrer equation ($D = K\lambda/\beta\cos\theta$). The results show that MgO NPs, were gained with an average diameter of 18 nm (Figure 2.). With this catalyst synthesis time in the microwave method than reflux method was very short and very high value products. FTIR was carried out with the range of 400 - 4000 cm^{-1} using IR Spectrophotometer Perkin-Elmer 783. A plausible mechanism for the preparation of 1, 2, 4-Triazine-5-ones derivative compounds using Nano MgO is shown in (Figure 3).

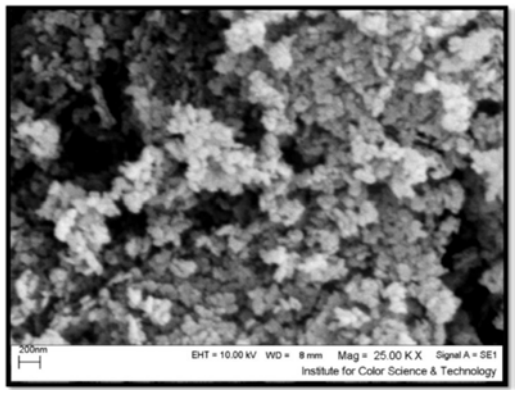


Figure 1. SEM image of the MgO nanoparticles.

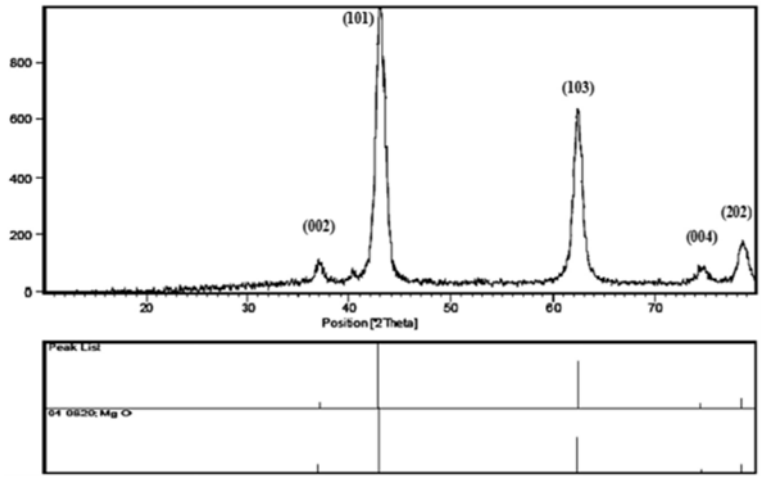


Figure 2. XRD scattering patterns of MgO nanoparticles.

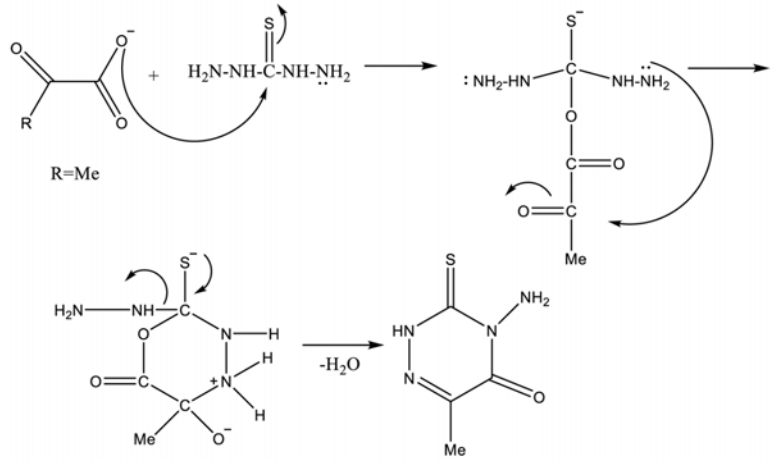


Figure 3. Possible mechanism for the synthesis of 1, 2, 4-Triazine-5-ones derivative in the presence of Nano-MgO.

3.1 FTIR Analysis

FTIR Spectra of MgO particles are shown in Figure 4. Peaks at 3664 cm^{-1}, 3448 cm^{-1} corresponding to the O-H stretching mode of hydroxyl groups were present on the surface due to moisture. Peak at 1672 cm^{-1} was attributed to the bending vibration of water molecule. The major peaks at 449 cm^{-1}, 511 cm^{-1}, 584 cm^{-1}, 671 cm^{-1} which confirmed the presence of Mg-O vibrations.

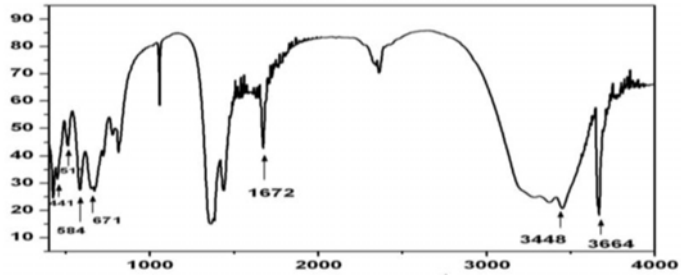


Figure 4. FTIR spectrum of MgO nanoparticles.

4. CONCLUSION

The aim of this work is to synthesize some 1, 2, 4-Triazine-5-ones derivative compounds utilizing the novel method in organic synthesis, microwave assisted organic synthesis (MAOS), and comparing the effectiveness of this method with conventional synthetic methods. This technology opens up new fortuities to the synthetic chemist, and especially for reactions that are not possible using conventional heating, improved reaction yields, decreased reaction times and even solvent free reaction conditions. This study describes a successful approach for the synthesis of 1, 2, 4-Triazine-5-ones derivative compounds using a domestic microwave oven. In conclusion, a simple and efficient method for the synthesis of 1, 2, 4-Triazine-5-ones derivative compounds has been explored. Mild reaction conditions, shorter reaction time, easy and low power consumption and excellent yields are main advantages of this method, which makes it an attractive and useful contribution to the present methodologies. The results show that the reaction in the microwave and using the catalyst in the period of 5-30 minutes are done. The same thermal conditions in the reaction time is 9 hours.

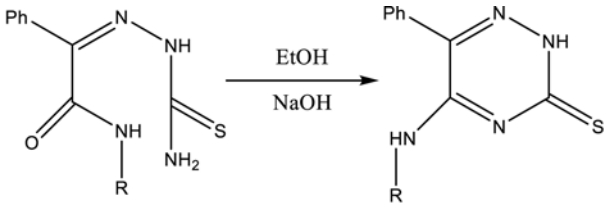
Recently, One of the methods used to prepare 1, 2, 4-Triazine or its derivatives is thiosemicarbazide with different reagents under the reaction leading to the formation of 1, 2, 4-Triazine is relevant. Density thiosemicarbazide and RNHCOCOPh in the presence of ethanol and acetic acid, intermediate thiosemicarbazide, which in the presence of alcoholic profit corresponding to 1, 2, 4-Triazine becomes (Scheme 5.). Reaction thiosemicarbazide and alpha di ones derivatives of also 1, 2, 4-Triazine is produced (Scheme 6.). Based on the same principle, we describe here the synthesis of 1, 2, 4-triazines starting from 1, 2-dicarbonyl and hydrazinecarbothioamide compounds. The reaction was also carried out under microwave irradiation. The results of the conventional process and the microwave irradiation process were compared which revealed that the latter process gave a comparatively higher yield in a shorter reaction time. This study describes a successful a roach for the synthesis of 4-[(tri fluorine methyl)-2, 6-di nitro phenyl amino]-4, 3-di hydro-6-methyl-3-thioxo-1, 2, 4-Triazine-5-ones derivatives using a domestic microwave oven (Table 1.). The results show that the highest yield of compound XIV was obtained at 96% intensity. Under the same reaction conditions, microwave conditions 1, 2, 4-Triazine reaction to these products by 54-96% in the period between 5-10 minutes went ahead. One advantage of this method is its large scale amicability and the results were comparable to the small scale experiments. Microwave assisted organic synthesis is a novel synthesis method developed over the past decade. Many scientists work across an array of disciplines that rapid heating with microwave technology has helped a number of processes. These include the preparation of samples for analysis, application to waste treatment, polymer technology, and drug release/targeting, decomposition processes, preparation of ceramics and hydrolysis of proteins and peptides. This technology opens up new ways to synthesize scientists, especially for reactions that are not possible using conventional heating, improved reaction yields, decreased reaction times and even solvent free reaction conditions. It is likely that with increased activities in this exciting area, widespread acceptance of this technology will result in the microwave oven becoming an integral part of every modern organic synthesis laboratory In conclusion, a simple

and efficient method for the synthesis of 4-[(tri fluorine methyl)-2, 6-di nitro phenyl amino]-4, 3-di hydro-6-methyl-3-thioxo-1, 2, 4-Triazine-5-ones derivatives has been explored. Mild reaction conditions, shorter reaction time, easy and quick isolation of the products, low power consumption and excellent yields are main advantages of this method, which makes it an attractive and useful contribution to the present methodologies.

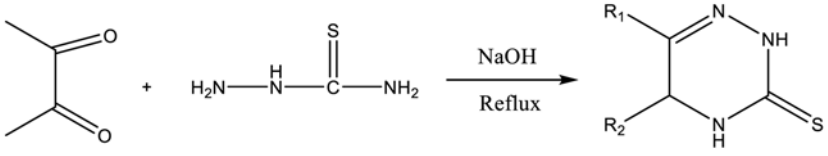
Table 1. Preparation of 1, 2, 4-Triazine-5-ones derivatives.

Entry	Products	R_1	Yields [a], (%)		Time		Mp, (°C)
			method *a* (M.W)	method *b* (r.t)	MW (Sec.)	Conv (Hrs.)	found, %
1	I	…….	94	85	180	3	170-173
2	II	CH_3	92	90	240	4	182-184
3	III	C_2H_5	92	91	300	6	140-145
4	IV	6-OCH_3	76	65	360	5	193-195
5	V	6-C_6H_5	56	43	300	5	121-124
6	VI	6-MeC_6H_4	75	70	180	7	142-144
7	VII	6-(4-EtC_6H_4)	81	62	240	9	193-195
8	VIII	6-(4-$OEtC_6H_4$)	54	33	300	6	198-200
9	IX	6-(4-OHC_6H_4)	91	79	360	4	226-228
10	X	6-(4-ClC_6H_4)	77	53	270	6	235-237
11	XI	6-(4-$NMe_2C_6H_4$)	90	86	340	8	219-221
12	XII	6-(4-$COCH_3C_6H_4$)	61	53	220	7	153-155
13	XIII	6-CH_3	65	60	350	8	196-198
14	XIV	6-C_6H_5	96	78	360	8	202-204
15	XV	6-OCH_3	82	64	370	9	201-203

[a,b] Yields refer to the pure isolated products.



Scheme 5. Density thiosemicarbazide.



Scheme 6. Reaction thiosemicarbazide and alpha di ones.

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