

SYNTHESIS OF 5-(3-METHYL BENZOFURAN-2-YL)-2-THIOL-1,3,4 OXADIAZOLE AND ITS PHOTOCHEMICAL STUDY: A BENZOFURAN DERIVATIVE

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Abstract

In the present work, new benzofuran derivative was synthesized and subjected to photochemical reaction. The structure of the product was characterized by spectral data.

Keywords: Synthesis, Photochemical reaction, Benzofuran derivative.

INTRODUCTION

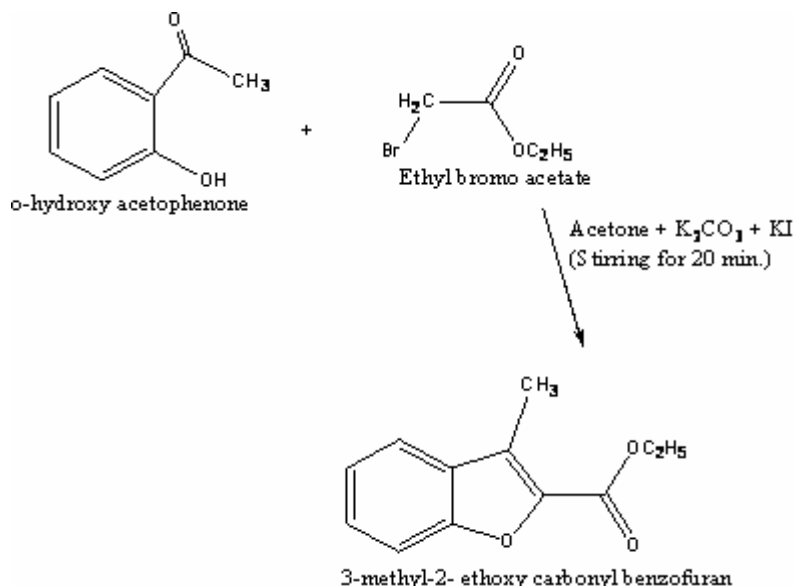
Benzofuran compounds are ubiquitous in nature, particularly among plant kingdom. Often such natural products possessing benzofuran nucleus are endowed with useful pharmacological properties. This has generated enormous interest in synthetic products containing benzofuran nucleus and has resulted in the development of benzofuran chemistry during the last several years. Due to wide scope for synthetic investigation leading to more potent synthetic leads, voluminous synthetic work has been done. Several benzofuran compounds are reported to possess antibacterial¹⁻⁴, antifungal², antitumor⁵⁻⁶ anti-inflammatory⁷, antidepressant⁸, analgesic⁹ and hypoglycemic¹⁰ activities. Substituted triazoles have been reported for antimicrobial¹¹⁻¹⁴ activity. The substituted oxadiazoles are heterocyclic compounds, which serve both as biomimetic and reactive pharmacophores and many are key elements with potential biological activities such as CNS stimulant, anti-inflammatory, hypotensive, insecticidal, bactericidal, hypoglycemic, analgesics, anticonvulsive, antiemetic, and diuretic, muscle relaxant and fungicidal activities.

MATERIALS AND METHODS

All the melting points were determined in open capillaries. Thin layer chromatography was performed on microscopic slides (2x7.5cm) coated with silica-Gel-G and spots were visualized under resembling iodine. IR spectra of all compounds were recorded in KBr on FT-IR spectrophotometer using KBr. The ^1H -NMR was recorded on Bruker advanced NMR400MHz instruments using CDCl_3 as solvent. Mass spectra were obtained using mass spectrometer.

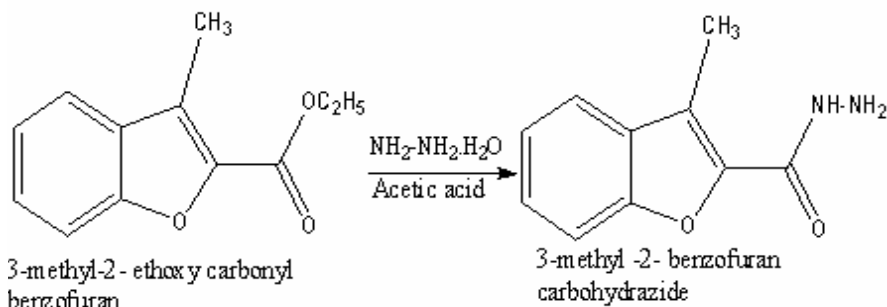
Preparation of 3-methyl-2-ethoxy carbonyl benzofuran:

o-hydroxy acetophenone (3ml) was taken in round bottom flask and 10ml of acetone and K_2CO_3 (3gm) crystals were added to it, the reaction mixture was stirred for 5 minutes in ice-bath. To this reaction mixture ethyl bromo acetate (2.8ml) was added drop by drop from dropping funnel about 10 minutes. Further whole reaction mixture was allowed to stir for 20 minutes with catalytic amount of potassium iodide. The resultant solution was poured in crushed ice, the solid obtained was filtered and recrystallized from ethanol to produced 3-methyl-2-ethoxy carbonyl benzofuran.



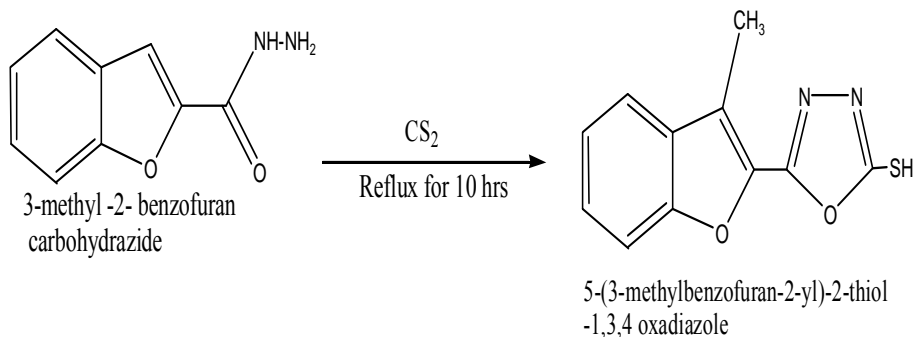
Preparation of 3-methyl-2-benzofurancarbohydrazide:

3-methyl-2-ethoxy carbonyl benzofuran (3gm) was taken in a round bottom flask and dissolved in 25ml ethanol and catalytic amount of acetic acid. To this solution, hydrazine hydrate (1ml) was added drop wise. The mixture was stirred at room temperature for about 2 hours. After completion of the reaction as indicated by thin layer chromatography (1:1::Benzene:Hexane solvent system), the 3-methyl-2-benzofurancarbohydrazide formed was recrystallized from ethanol.



Synthesis of 5-(3-methyl benzofuran-2-yl)-2-thiol -1,3,4 oxadiazole :

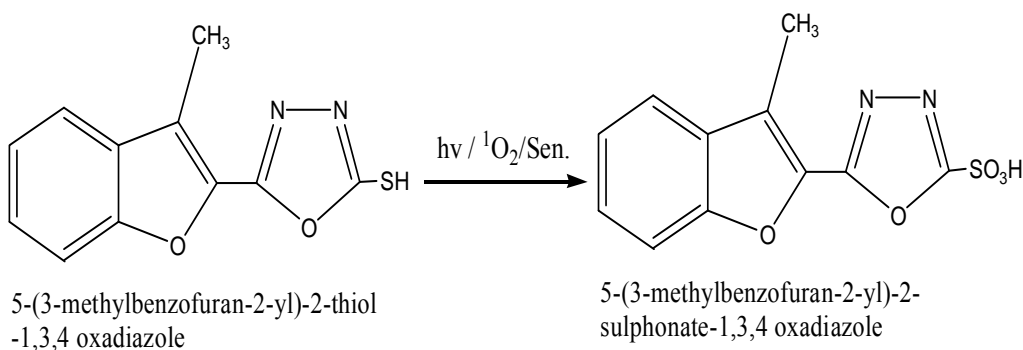
3-methyl-2-benzofurancarbohydrazide (1.9gm) was refluxed with alcoholic potassium hydroxide (0.56 gm) and carbon disulphide (10 ml) for 10 hours. TLC was taken at regular intervals (1:1::Benzene:Hexane solvent system) . The reaction mixture then cooled and acidified with concentrated HCl. The compound 5-(3-methyl benzofuran-2-yl)-2-thiol -1,2,3 oxadiazole separated as solid and was filtered , washed with cold water and recrystallised using dimethyl formamide - methanol mixture. Yield: - 2.5gms, Melting Point: - 200⁰C was reported.



Photochemical reaction of 5-(3-methyl benzofuran-2-yl)-2-thiol-1, 3, 4 oxadiazole with ultraviolet light:

A sample of 5-(3-methyl benzofuran-2-yl)-2-thiol-1,3,4 oxadiazole (0.5gms) was dissolved in a small volume of dry benzene and then made up to 500 ml of benzene. Benzophenone (0.01gm) was added to the solution as sensitizer. The solution was irradiated with a low pressure mercury lamp, which had been placed inside the immersion well. Progress of the reaction was followed by TLC analysis (1:1::Benzene:Hexane solvent system). After 10 hrs no new product were observed and starting compound was recovered unchanged. Again taken sample of 5-(3-methyl benzofuran-2-yl)-2-thiol-1,3,4 oxadiazole (0.5gms) was dissolved in doubly distilled water (100ml) and distilled benzene (100ml) in double walled beaker.

Benzophenone (0.01gm) was added to the solution as sensitizer. The solution was irradiated with a low pressure mercury lamp, which had been placed inside the immersion well. Air was continuously bubbled through the solution with the help of an aerator. The temperature of the reaction mixture was kept constant by continuous water circulation. Progress of the reaction was followed by TLC analysis (1:1::Benzene:Hexane solvent system). Starting material was almost completely consumed in 10 hrs. Solvent was removed under reduced pressure and residue was chromatographed over silica gel. Elution of the column with a mixture (8:2) of benzene and hexane gave a new product identified as the 5-(3-methyl benzofuran-2-yl)-2-sulphonate -1,3,4 oxadiazole. Yield :- 0.3 gms, Melting Point :- 254-256⁰C was reported.



RESULTS AND DISCUSSION

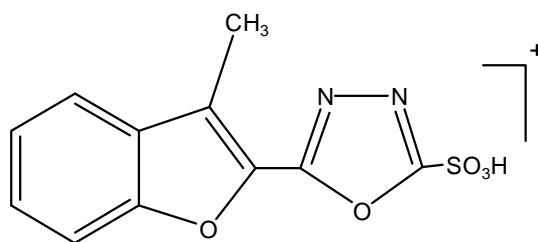
Characterization Data of the Synthesized Compound: 5-(3-methyl benzofuran-2-yl)-2-thiol -1,3,4 oxadiazole:

The IR spectra (KBr) of the compound shows absorption at 1047.27 cm⁻¹, 2842.88 cm⁻¹, 2738.73 cm⁻¹, 1608.52 cm⁻¹, 2974.03 cm⁻¹ due to C-O-C, aromatic CH, C-SH, C=N, -CH₃ stretch respectively.

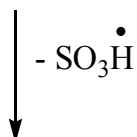
The ¹HNMR in CDCl₃ shows in the region 8.03 δ (1H) due to SH, 1.78 δ (3H) due to furan-CH₃, 7.30-7.63 δ (4H) due to aromatic-H.

The Mass spectrum shows molecular ion peak at m/z 232 (Molecular formula- C₁₁H₈N₂O₂S).

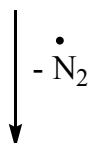
The fragmentation pattern is as follows: - Molecular formula- C₁₁H₈N₂O₅S



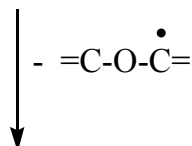
m/z 280



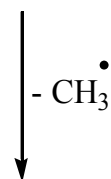
m/z 199



m/z 171



m/z 131



m/z 116

The fragmentation pattern of 5-(3-methyl benzofuran-2-yl)-2-sulphonate -1,3,4 oxadiazole

Characterization Data of the Synthesized Compound: 5-(3-methyl benzofuran-2-yl)-2-sulphonate -1,3,4 oxadiazole:

The IR spectra (KBr) of the compound shows absorption at 1045.35 cm⁻¹, 2839.02 cm⁻¹, 1334.65 cm⁻¹, 1608.52 cm⁻¹, 2974.03 cm⁻¹ due to C-O-C, aromatic CH, S=O, C=N, -CH₃ stretch respectively.

The ¹HNMR in CDCl₃ shows in the region 2.2 δ (1H) due to SO₃H, 1.74 δ (3H) due to furan-CH₃, 7.56 δ (4H) due to aromatic-H.

The Mass spectrum of 5-(3-methyl benzofuran-2-yl)-2-sulphonate -1,3,4 oxadiazole exhibits the molecular ion peak at m/z 280, which is the molecular weight of the compound and other fragments at m/z 199, 171, 131, 116.

CONCLUSION

The purpose of present work was to synthesized, characterized and study the Photochemical reaction of benzofuran derivative during this period I was able to successfully synthesized derivative and study its photochemical reaction. The compounds were characterized by melting point, TLC, FT-IR, ^1H NMR and Mass spectral analysis.

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