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International Journal of Current Research
Vol. 7, Issue, 08, pp.19507-19510, August, 2015

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

ISSN: 0975-833X

RESEARCH ARTICLE

STUDIES IN THE SYNTHESIS OF SUBSTITUTED 4-DIMETHYLAMINO-BENZOINHYDRAZONE

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ARTICLE INFO

Article History:
Received 27th May, 2015
Received in revised form
15th June, 2015
Accepted 10th July, 2015
Published online 31st August, 2015

Key words:
4-Dimethylaminobenzoin,
Sodium hydroxide,
Dioxane-water (80%) medium,
Substituted benzoin hydrazones,
4,4'-dimethoxy benzoin hydrazone

ABSTRACT

Recently the synthesis of 4-dimethylaminobenzoinhydrazone were carried out by the condensation of 4-dimethylaminobenzoin with hydrazine hydrate in presence of aqueous sodium hydroxide in Dioxane-water (80%) medium respectively. Similarly 4,4'-dimethoxy benzoin hydrazone were synthesized by the interaction of 4,4'-dimethoxy benzoin with hydrazine hydrate in presence of aqueous sodium hydroxide in dioxane-water (80%) medium respectively. The synthesis of 4-dimethylaminobenzoin and 4,4'-dimethoxybenzoin were carried out by the known literature method. The structure of all the synthesized compounds were justified on the basis of chemical characteristics, elemental and I.R. and NMR spectral analysis.

***Citation*:** Dahikar, P. M., 2015. "Studies in the synthesis of substituted 4-dimethylamino-benzoinhydrazone", *International Journal of Current Research*, 7, (8), 19507-19510.

INTRODUCTION

Benzoinhydrazone are well known for their bacterial activity coordination compounds containing donor atoms are reported to possess antimicrobial activity (Pettering and Crime, 1967). Shcherbakov *et al*. (2009) carried out specificity of complex formation of Benzoin (Phthalazin-1-Yl) hydrazone with copper(II) and nickel(II). A series of quinoxalinone derivatives were synthesized and studied their antimicrobial and antiinflammatory activities were studied by Khan *et al*. (2009). Synthesis of o-amino-acetophenone o-hydroxybenzoylhydrazone complexes of divalent transition metals and studied their spectral and antimicrobial activities was reported by Nawar *et al*. (2000). A structural analysis of salicylaldehyde benzoyl hydrazone by using a combination of NMR, IR and theoretical investigation was carried out by Cordier *et al*. (2004). The simultaneous spectroscopic determination of palladium and osmium with salicylaldehyde hydrazone was carried out by Ray *et al*. (1979). The synthesis and structural characterization of three new co-ordination complexes of Co(II), Mn(II) and Cu(II) with N,N,O-donor hydrazine ligands were carried out by Shit *et al*. 2009 The synthesis, magnetic, spectral, thermal and biological studies of Ti(III), Vo(IV), Cr(III), Mn(II), Fe(III) and Zr(IV) complexes with chelating hydrazine derived from 2-hydroxy-5 methylacetophenone and furoic acid hydrazide carried out by Dhande *et al*. (2007). Thermal analysis in structural characterization of hydrazone ligands and their complexes studied by Andyelkovic *et al*. (2001). The synthesis of novel(II) complexes with new ligand derived from hydrazone of isoniazid and their magneto-spectral, electrochemical, thermal and antimicrobial investigation were studied by Prasad *et al*. (2008). The important reaction of carbonyl with various hydrazines were briefly studied in presence of strong bases in ethanol medium (Pavia *et al*., 2004; Hegde *et al*., 2007; Hassan *et al*., 2005 and Silverstein *et al*. 4th Ed.,

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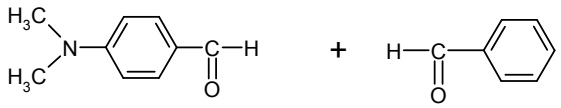
Experimental

The melting point of the all the synthesized compounds were recorded using hot paraffin bath the carbon and hydrogen analysis were carried out on Carlo-Ebra 1106 analyser. Nitrogen estimation was carried out on Colman-N-analyzer-29. IR spectra were recorded on Perkin Elmer spectrometer in range 4000-400 cm^{-1} in KBr pellets. PMR spectra were recorded on Brucker AC 300F spectrometer with TMS as internal standard using $CDCl_3$ and DMSO-d_6 as solvent. The purity of compounds was checked on silica Gel-G pellets by TLC with layer thickness of 0.3 mm. All chemicals used were of AR grade.

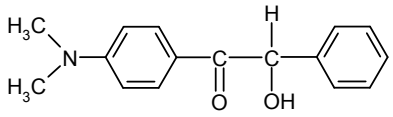
Scheme – I



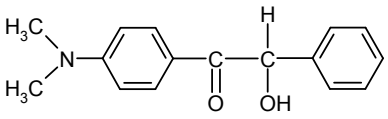
(I)
4-Dimethylaminobenzaldehyde

(II)
Benzaldehyde

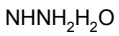
i) NaCN
ii) Reflux for 3 hrs in dioxane-water medium



(III)
4-Dimethylaminobenzoin

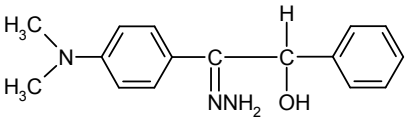


(III)



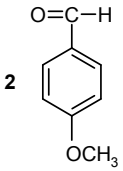
(IV)
Hydrazine hydrate

i) aq. NaOH
ii) Reflux for 3 hrs in dioxane-water medium



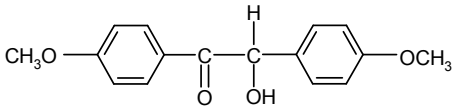
(V)
4-Dimethylaminobenzoinhydrazone

Scheme – II



(IV)
Anisaldehyde

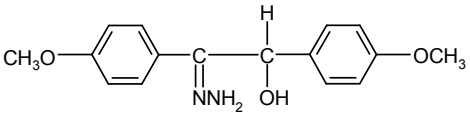
i) Reflux for 3 hrs in dioxane-water medium
ii) Poured in ice-cold water



(V)

(VII)
4,4'-Dimethoxybenzoin

i) aq. NaOH
ii) Dioxane-water medium
iii) Poured in ice-cold water



(VIII)
4,4'-Dimethoxybenzoinhydrazone

Preparation of 4-dimethylaminobenzoin (III)

4-Dimethylaminobenzoin (III) was prepared by refluxing benzaldehyde (I), 4-dimethylaminobenzaldehyde (II) and NaCN in 80% dioxane-water medium for one hour on water bath. This reaction mixture was poured in ice-cold water to obtain sticky semisolid. The sticky product was kept in dessicator containing anhydrous calcium oxide for half an hour, after that it was dissolved in alcohol. The alcohol was distilled off to isolate yellowish product. It was again refluxed in 80% dioxane-water medium on water bath for one hour and the reaction mixture was again poured in ice-cold water. After acidification with dilute hydrochloric acid, the yellow crystals were obtained, they were recrystallized with alcohol, yield 78%, m.p. 150°C (Scheme-I).

Examination of the product

It is yellow crystalline solid having m.p. 150°C. It gave positive test for nitrogen. It gave satisfactory elemental analysis. As this compound is known the spectral analysis was not carried out.

Synthesis of 4-dimethylaminobenzoinhydrazone (V)

4-Dimethylaminobenzoinhydrazone (V) was synthesized by refluxing 4-dimethylaminobenzoin (III), hydrazine hydrate (IV) in 1:1 molar proportion in presence of aqueous sodium hydroxide in dioxane-water mixture for half an hour. This reaction mixture was then poured in ice-cold water to obtain yellow coloured 4-dimethylaminobenzoinhydrazone, yield 78%, m.p. 150°C.

Elemental Analysis

C [(found 70.52%) calculated 71.37], H [(found 6.63% calculated 7.06%], N [(found 15.61% calculated 15.61].

IR Spectra

The spectra was carried out in KBr pellets and the important absorption can be correlated as (cm^{-1}) 3423 (O–H stretching), 3064.2 (Ar–H stretching), 1597.2 (C=N stretching in hydrazine), 1388 (C–O stretching).

NMR Spectra

The spectrum was carried out in $CDCl_3$ and DMSO-d_6. This spectrum distinctly displayed the signals due to Ar–H protons at 7.82-7.22 ppm Ar–R–OH protons at δ 5.84 ppm, –CH proton at δ 2.16 and $–CH_3$ protons at δ 3.085-3.014 ppm.

Preparation of 4,4'-dimethoxybenzoin (VI)

4,4'-Dimethoxybenzoin (IV) was synthesized by refluxing anisaldehyde (V) and NaCN in 80% dioxane-water medium for 2 hrs on water bath. This reaction mixture was poured in acidic ice-cold water. The yellow crystalline was obtained. Keeping anhydrous calcium carbonate for one hr then the sticky product was recrystallized by alcohol, yield 80%, m.p. 198°C. (Scheme-II)

Examination of the product

It is yellow crystalline solid having m.p. 198°C. It gave positive test for alcoholic group. It gave positive test with sodium bisulphate, which clearly indicates presence of carbonyl group. It gave satisfactory elemental analysis for carbon and hydrogen. As the compound was known and gave satisfactory chemical and elemental analysis. Hence, further spectral study was not carried out.

Synthesis of 4,4'-dimethoxybenzoin hydrazone (VII)

4,4'-Dimethoxybenzoin hydrazone (VIII) was synthesized by refluxing 4,4'-dimethoxybenzoin (VII), hydrazine hydrate (V) in 1:1 molar proportion in presence of aqueous sodium hydroxide in dioxane-water mixture for 3 hrs. This reaction mixture was poured in ice-cold water, to obtain yellow coloured crystals of 4,4'-dimethoxybenzoin hydrazone (VI). It was crystallized by alcohol, yield 80%, m.p. 130°C.

Elemental Analysis

C [(found 66.28%) calculated 67.13], H [(found 5.23% calculated 6.29%], N [(found 9.79% calculated 9.79].

IR Spectra

The spectra was carried out in KBr pellets and the important absorption can be correlated as (cm^{-1}) 3388 (O–H stretching), 3010.7 (Ar–H stretching), 1169.6 (C–N stretching), 1634 (C=N stretching in hydrazone), 1362.1 (C–O stretching).

NMR Spectra

The spectrum was carried out in $CDCl_3$ and DMSO-d_6. This spectrum distinctly displayed the signals due to Ar–H protons at 7.9088-7.2365 ppm, $–OCH_3$ protons at δ 3.8180-3.7549 ppm, imino proton at δ 6.8696-6.8325 ppm, –OH proton at δ 5.848 ppm and –CH protons at δ 2.1704 ppm.

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