Synthesis And Characterization of 5-(Mercapto-1,3,4-Thiadiazole-2yl)α,α-Diphenyl Methanol From Benzilic Acid

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Received in : 31 December 2007 , Accepted in : 25 June 2008

Abstract

5-(mercapto-1,3,4-thiadiazole-2yl)α,α-(diphenyl)methanol have been synthesized by ring closer of potassium xanthate[which have been prepared by reaction of benzilic acid hydrazide with carbon disulphide in potassium hydroxide] using conc.sulphuric acid at (0-5)°C scheme(I).

Their characterization was carried out from T.L.C, M.P, FT.IR and ^{1}H-NMR.

Key wared: 1,3,4-thiadiazole derivative.

Introduction

1,3,4-Thiadiazole is one of a class of organic heterocyclic compounds containing a five member diunsaturated ring structure composed of two nitrogen atoms at positions (3 and 4) and one sulphur atom at position [1].

Most of published work on the four thiadiazoles has been on the 1,3,4–thiadiazoles. Physical, theoretical, and spectroscopic properties have been reviewed[2,3,4,5].

A useful preparative method for 2–amino– 5-mercapto–1,3,4–thiadiazole was developed by Guha[6] which showed that when thiosemicarbazide is treated with carbon disulphide and potassium hydroxide, the potassium salt of thiosemicarbazide–4–dithio carboxylic acid (Xanthate) was formed.

Hiremarth et.al[7] synthesized a series of 2–amino–5–[4– (substituted) anilino]–methyl–1,3,4–thiadiazole through cyclo condensation of thiosemicarbazide derivative with phosphoric acid.

Zamani et.al.[8] synthesized new 1,3,4–thiadiazole derivatives.

Kurzer and Secker[9] found that the use of reactants incorporating free hydrazine group provided a versatile route to substituted 1,3,4–thiadiazole.

They reported various approaches, employing the prototype hydrazine it self and some of its simple congeners.

OnkoL et.al[10] synthesized1,3,4–thiadiazole by ring closer some compounds by use conc. Sulphuric acid at (0-5)°C

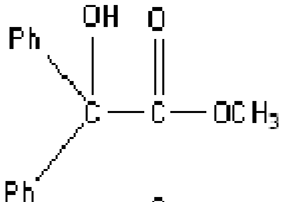
In this work we have been synthesized 1,3,4-thiadiazole by treated potassium xanthate with conc sulphuric acid at (0-3)°C. the products were characterized by T.L.C, M.P, FT.IR and ^{1}H-NMR spectral data.

Instruments

Melting points were recorded using hot stage Gallenkamp melting point apparatus and were uncorrected. Thin layer chromatography (T.L.C) was carried out using fertigfollen precoated sheets type polygram silica-gel as stationary phase ethyl acetate as eluent, and the plates were developed with iodine vapor. Infrared spectra were recorded using Fourier transform infrared SHIMADZU (8300) (FT.IR) infrared spectrophtometer, KBr disc or thin film was performed by CO.S.Q.C IRAQ. ^{1}H NMR, 13C– NMR and Mass spectra were recorded on Foruier Transform Varian spectrometer, operating at 300 MHz with tetramethylsilane as internal standared in DMSO, Measurments were made at Chemistry Department, Al– Al-Bayt University, Jordan.

Experimental

Synthesis of methyl α-hydroxy-α,α-(diphenyl) acetate [2]



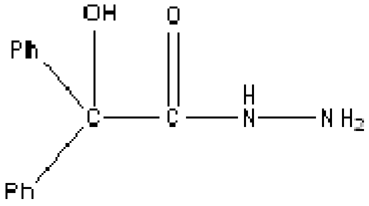
2

A mixture of benzilic acid [1] (2g, 0.08mol.) and (0.9g, 0.08mol.) of anhydrous sodium carbonate was dissolved in (20 ml) dry acetone. To this solution (1.1g, 0.08mol.) of dimethyl sulphate was added.The resulting mixture was heated under reflux for 4 hr.

The reaction mixture was then allowed at cool down to room temperature, the reaction was followed by (T.L.C)*, extraction with ethyl acetate and evaporation of the dried organic layer, the product was white Crystille, recrystillized from ethanol (1.82 g, yield 86%, m.p= 50– 52°C).

* Silica gel as stationary phase
Ethyl acetate as eluent

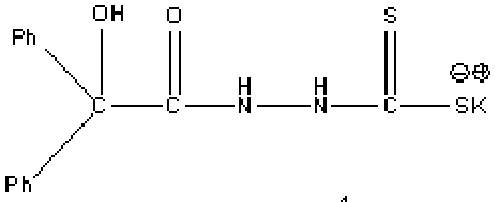
Synthesis of α-hydroxy-α,α-diphenyl acid hydrazide[11](3).



3

Compound [3] was synthesized by addition of the hydrazine monohydrate 98% (0.2g, 0.004mol.) to methyl ester [2] (1g, 0.004mol.). with stirring, then the absolute ethanol (10 ml) was added and refluxed until the precipitate formed(1.5 hrs). After cooling, the precipitate was filtered off and recrystallized from ethanol, (0.74g) yield 74%, m.p. 150°C.

Synthesis of potassium xanthate[12](4).



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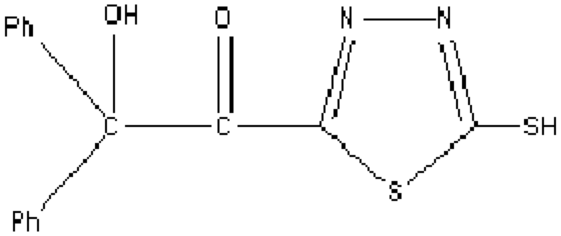
(1g, 0.004mol.) of acid hydrazide (3) was dissolved in absolute ethanol 99.9% (10 ml) with (0.23g, 0.004mol.) of potassium hydroxide. The mixture was stirred for 15 minute then (0.31g, 0.004mol.) of carbon disulphide was added, and continue stirring for 24 hrs. at room temperature, the precipitate was filtered and dried, washed with ether, yield (0.74g, 50%), mp (280°C dec.) .

Synthesis of 5-(mercapto-1,3,4-thiadiazole-2yl) (diphenyl) methanol[5].

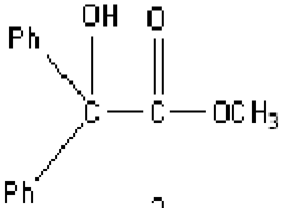


5

Potassium xanthate (4) (0.76 g, 0.002 mol.) was dissolved in distilled cold water and then carefully acidified with conc. Sulphuric acid (H_2SO_4) 98% at (0–5)°C until the precipitate formed. The precipitate was filtered and dried, recrystillization from ethanol. Yielding comp. (5) (0.42 g, 66%) m.p 122–124°C.

Result and Discussion

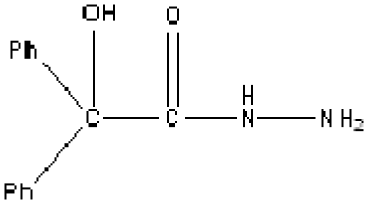
Synthesis and identification of methyl α-hydroxy-α,α-(diphenyl) acetate [2].



2

The benzilic acid was converted to methyl-α-hydroxy-α,α- (diphenyl) acetate (2) by the common esterification process, using dimethylsulphate in presence of anhydrous sodium carbonate in dry acetone.The (2) was identified by T.L.C, m.p and FT.IR spectra, which showed the disappearance of the absorption band at 1720 cm^{-1} which is due to stretching vibration of the carbonyl group of the acid, while appearance of the characteristic absorption band at 1722 cm^{-1} due to stretching vibration of the (C=O) for the forming ester, also disappearance of the wide absorption bands at the region (2838–3560) cm^{-1} which belongs to the stretching vibration of (-OH) group for the benzilic acid also appearance band at 1168 cm^{-1} due to (–O–CH3) of methyl benzilate ester.

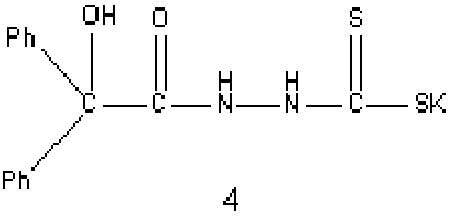
Synthesis and identification of α-hydroxy-α,α-diphenyl acid hydrazide[3].



3

The reaction of hydrazine hydrate in absolute ethanol . most common reactions to synthesize the acid hydrazide derivatives. The hydrazide derivatives were identified by m.p and FT.IR spectra which showed the appearance of the characteristic absorption band at the region (3251–3300) cm^{-1} due to the asymmetric and symmetric stretching vibration of the ($–NH–NH_2$) group, the FT.IR also showed the disappearance of absorption bands at the region 1722 cm^{-1} due the stretching vibration of carbonyl group of ester, while a new band appeared at the region 1700 cm^{-1} due to stretching vibration of amide band., also appearance band at 1537 cm^{-1} due to bending vibration of (N–H) moiety.

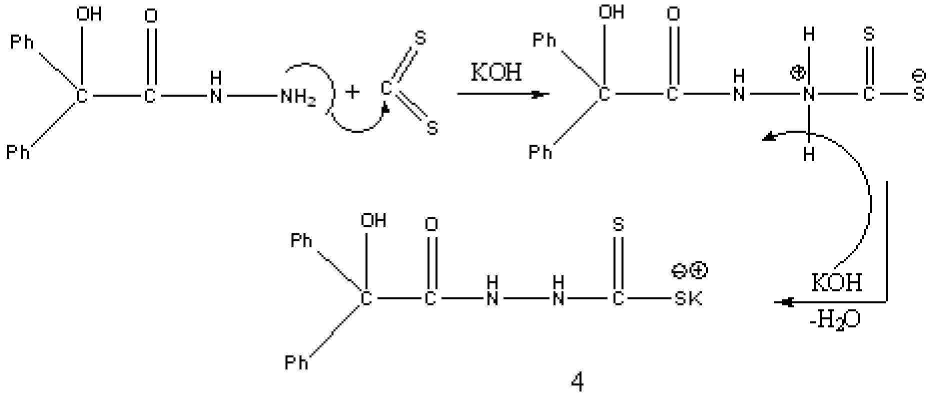
Synthesis and identification of potassium xanthate [4].



4

The acid hydrazide was treated with carbon disulphide in potassium hydroxide to afford the salt as in the following mechanism[14].

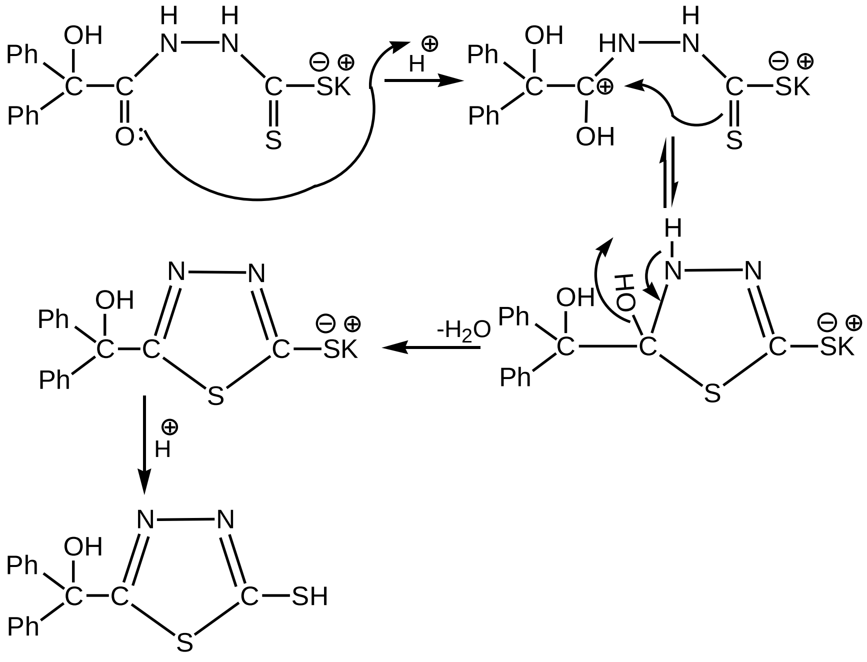
The compound (4)identified by m.p and FT.IR spectra, the FT.IR spectra showed the disappearance of absorption band at the (3251–3300) cm^{-1} due to the asymmetric and symmetric stretching vibration of the (–NH–NH_2) group, appearance band at 1049 cm^{-1} due to bending vibration of (C=S)(15), also appearance band at (1448–1492) cm^{-1} due to (–N–C=S)(16) stretching vibration this band according strong evidence to presence the potassium xanthate and also appearance band at 1614 cm^{-1} due to (C=O) amide while disappearance band at 1700 cm^{-1} due to (C=O) of α–hydroxyl–α,α–diphenyl acetohydrazide (3) this two evidence to presence this reaction.



4

Synthesis and identification of 5–(mercapto–1,3,4– thiadiazole–2–yl) (diphenyl) methanol (5).

The addition of sulphuric acid 95–98% at (0–3) °C lead to the cyclization which produce the thiadiazole (5) as in the following suggest mechanism[17]:



[S31]

The compound [5] was identified by m.p. FT.IR, ^{1}H-NMR spectroscopy.

The FT.IR showed band 1060 cm^{-1} due to bending vibration of (C=S)[15] group, appearance band between (1685–1720) cm^{-1} due to stretching vibration of (C=N) group, also appearance very week band at 2478 cm^{-1} due to (S–H) group, appearance strong band at (1445–1496) cm^{-1} due to stretching vibration of (–N–C=S)[16], and appearance band at 3049 cm^{-1} due to (C–H) Aromatic.

^{1}H–NMR spectrum showed the following characteristics chemical shifts (DMSO as a solvent) were appeared: the singlet signal at δ 2.5 suggested the attribution to the proton of (O–H) group, while a singlet at δ 3.94 suggested the attribution to the proton of (S–H) group, [addition of D_2O caused the signal at δ 2.5 and δ 3.94 to disappear, Fig. (3.44)], the singlet signal at δ 7.3 suggesting the attribution of ten protons of two benzene rings.

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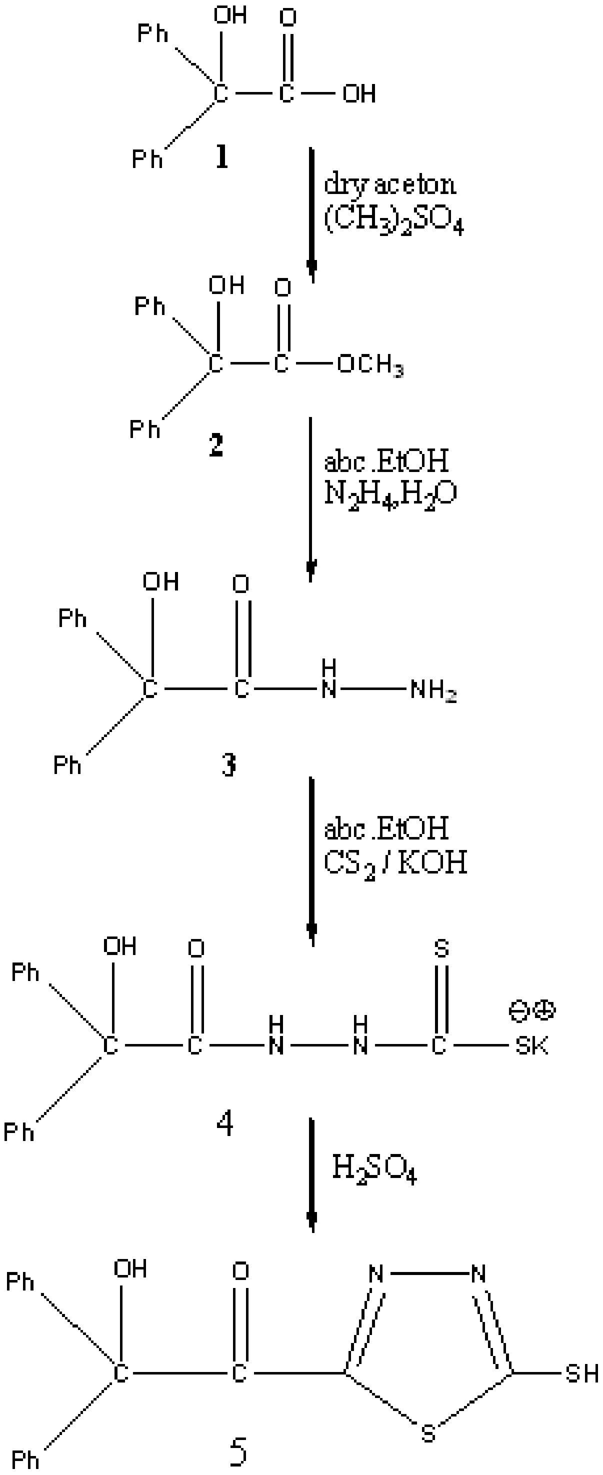
1
dry aceton
(CH3)2SO4
2
abc.EtOH
N2H4.H2O
3
abc.EtOH
CS2 / KOH
4
H2SO4
5

تحضير وتشخيص المركب 5-(مركبتو-4,3,1-ثايادايزول-2-يل)-α,α-ثنائي فنيل ميثانول من حامض البنزيلك

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استلم البحث في : 31 كانون الأول2007 ، قبل البحث في : 25 حزيران 2008

الخلاصة

حضر المركب 5-(مركبتو-4,3,1-ثايادايزول-2-يل)-α,α-ثنائي فنيل ميثانول بالغلق الحلقي لملح الزانثيت (الذي حضر من تفاعل مركب الهايدرازايد (المشتق من حامض البنزايلك) مع ثنائي كبريتيد الكاربون بوجود هيدروكسيد البوتاسيوم) مع حامض الكبريتيك المركز في درجة حرارة (صفر- 5) كما موضح في المخطط.

وشخصت المركبات المحضرة بكروموتوكرافيا الطبقة الرقيقة، درجة الانصهار، مطيافية الاشعة تحت الحمراء والرنين النووي المغناطيسي.

الكلمات المفتاحية : مشتق 4,3,1- ثايادايزول