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Synthesis , Characterization of Some Benzilyl HydrazoneDerived from Benzilic Acid Hydrazide

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الملخص

يتضمن البحث تحضير مركبات هيدرازونالبنزيليك (4a-g)و(5a-f) من خلال تكاثف معوضاتالاسيتوفينون وكذلك معوضاتالبنزوفينون مع هيدرازيد حامض البنزيليك , تم تشخيص الهيدرازونات المحضرة بواسطة الأشعة تحت الحمراء ,الرنين النووي المغنطيسي لكل من البروتون والكاربون وطيف الاشعة فوق البنفسجية بالاضافة الى القياسات الفيزياوية

ABSTRACT

Benzilyl hydrazones (4a-g) and (5a-f) were prepared from condensation of substituted acetophenone and substituted benzophenone with benzilic acid hydrazide . The structurale of the synthesized hydrazones are characterized by IR , ^{1}H-NMR ,^{13}C-NMR and UV spectroscopy, in addition of physical measurments.

Keywords: Benzilic acid , hydrazide , hydrazone

INTRODUCTION

It is well known that the hydrazones characterized by the presence of the tri atomic (-C=N-N-),these are distingushed from compounds by the presence of the two interlinked nitrogen atomes. Hydrazonesand their derivatives show a rersatile class of compounds in organic chemistry [1] ,these compounds have been found to posses many biologecal activities such as anticonvulsants [2],anti-inflammatory [3],antimalerial [4],antitumer [5],antiviral [6],antimicrobaial[7], antibacterial [8].

We have been interested in hydrazine chemistry for along time and various axes have been explored .We found that the hydrazones are tipically formed by the condensation of hydrazine or hydrazides with an aldehydes and ketones.[9,10]

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Thus ,We are use the benzilic acid hydrazide as starting material to prepare some hydrazones (4a-g) and (5a-f) via reaction with derivatives of acetophenone and benzophenone respectively.

EXPERIMENTAL

Melting point were determined in open capillary tube on stuartSMP30melting point apparatus.The IR spectra were recorded in KBr on FTIR-600 Bio Tec. Engineering Mangement Co.Ltd.(UK) using KBr discs.^{1}H-NMR and ^{13}C-NMR spectra were recorded on JEOL EEA 400MHZ FT-NMR.UV spectra were recorded on a shimadzu UV/Vis -1650 pc Spectrometer using chloroform as asolvent.

The methyl benzilate (2) was prepared by the usual esterfication method,benzilic acid hydrazide (3)was prepared using reported method[11]starting from methyl benzilate.

Preparation of2-Hydroxy-N- [1-substitutedphenyl)ethylidene]-2,2-diphenyl acetohydrazide[12] (4a-g):

To equimolar of benzilic acid hydrazide (0.24g,0.001mole) and substituted acetophenone (0.001mole)in absolute ethanol (30ml),(1ml) of acetic acid was added.The mixture was refluxed for six hours,Then cooled .The solid precipetate was filtered off and recrystallized from sutiable solvent.Physical and spectral data are listed in tables (1 and 3).

Table (1) :Some physical constants for compounds (4a-g)

Comp. No.	Ar	Molecular Formula	m.p C^0	Yield %	Colour	Cryst.solvent
4a	C_6H_5	$C_{22}H_{20}N_2O_2$	182-184	56	white	Ethanol
4b	p-ClC_6H_4	$C_{22}H_{20}N_2O_2Cl$	233-235	43	white	Ethanol+water
4c	p-$NH_2C_6H_4$	$C_{22}H_{22}N_3O_2$	148-150	63	Pale yellow	Methanol
4d	p-BrC_6H_4	$C_{22}H_{20}N_2O_2Br$	162-164	51	white	Ethanol+water
4e	p-OH C_6H_4	$C_{22}H_{21}N_2O_3$	165-167	45	yellow	Ethanol
4f	m-OHC_6H_4	$C_{22}H_{21}N_2O_3$	167-170	53	Pale yellow	Acetone
4g	o-OHC_6H_4	$C_{22}H_{21}N_2O_3$	178-181	56	yellow	Ethanol

Preparation of 2-hydroxy-N-[(1-substututedphenyl)phenylmethylene]2,2-diphenyl acetohydrazide[13] (5a-f):

A solution of benzilic acid hydrazide (0.02mole) in 25 ml of ethanol was added to an etanolic solution(25ml) of (0.02 mole) substituted benzophenone, the reaction mixture was refluxed on a water bath for 4h.,then cooled to room temperature.The resulting solid

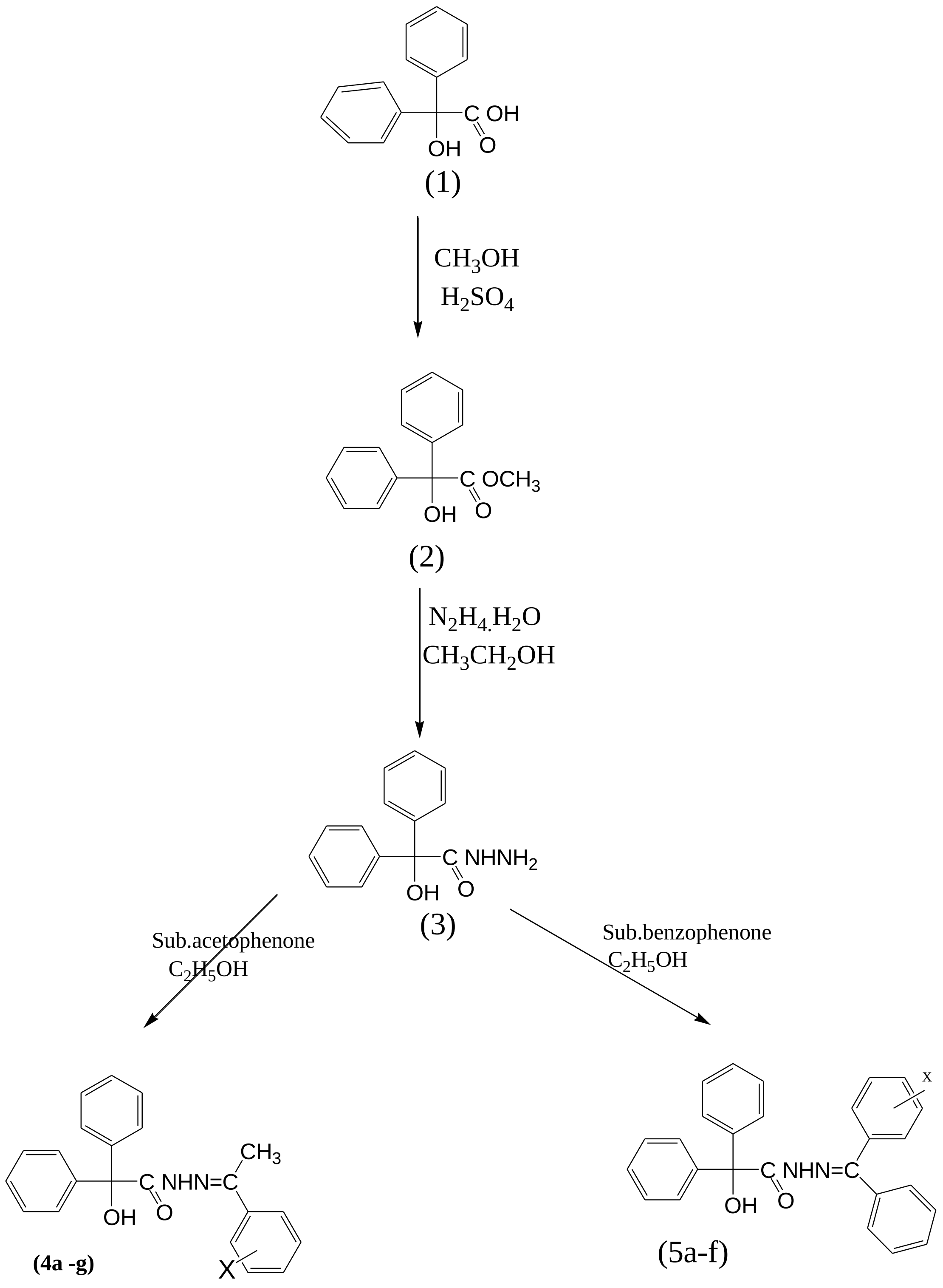
was dried, and recrystallized from sutiable solvent.Physical and spectral data are listed in (Table 2 and 4).

Table (2) :Somephysical constants for compounds (5a-f)

Comp. No.	Ar	Molecular Formula	m.p C^0	Yield %	Colour	Cryst. solvent
5a	C_6H_5	$C_{22}H_{20}N_2O_2$	161-163	55	white	Ethanol
5b	p-BrC_6H_4	$C_{27}H_{22}N_2O_2Br$	155-158	62	white	Methanol
5c	p-ClC_6H_4	$C_{24}H_{22}N_2O_2Cl$	118-120	61	Brown	Ethanol+Water
5d	2-OH-4-MeOC_6H_3	$C_{28}H_{24}N_2O_4$	157-159	61	yellow	Ethanol
5e	2,5-diMeO C_6H_3	$C_{29}H_{26}N_2O_4$	163-165	67	white	Methanol
5f	2,4-diMeO C_6H_3	$C_{29}H_{26}N_2O_4$	158-160	62	Pale yellow	Ethanol

RESULTS AND DISSCUSION

The synthetic procedures adopted are illasrated in schem 1.The starting material for the synthesis of hydrazones (4a-g) and (5a-f) is benzilic acid hydrazide(3) which was prepared by the reaction of benzilic acid with methanol in acidic media to form methyl benzilate(2) which was converted to corresponding hydrazide(3) by it is reaction with hydrazine hydrate in ethanol .Hydrazones (4a-g)and(5a-f) are readily prepared in good yield from benzilic acid hydrazide (3) with substituted acetophenone and benzophenone respectively.



X= $C_6H_5^-$,p-ClC_6H_4,p-$NH_2C_6H_4$,p-BrC_6H_4,p-OHC_6H_4,
m-OHC_6H_4,o-OHC_6H_4

X=C_6H_5,p-BrC_6H_4,p-ClC_6H_4,2-OH^{-4}-$MeOC_6H_3$,2,5-di$MeOC_6H_3$
2,4-di$MeOC_6H_3$

Schem 1

All products were charecterized by physical and spectral data.The IR spectra for compounds (4a-f) showed characteristic absorbtion peak in the reagion (1643-1655 cm^{-1}) stretching for (C=O amide) group , at (1581-1616 cm^{-1}) stretching group for (C=N) group , (3022-3077 cm^{-1}) and at (3248-3302 cm^{-1}) due to (NH)group.

The ^{1}H-NMR spectra for compounds (4a,4c,4d and 4e)in (DMSO-d_6) in ppm showed significant peaks as the following .singlet in the range(2.19-2.25ppm)due to CH_3 group,(2.15-2.25ppm)for hydroxyl group,also at the range(6.55-7.15ppm) due to NH group,while the aromatic of acetophenone partshowed multiplet in the range(6.35-7.82ppm) ,also the aromatic of part showed multiplet in the range(7.18-7.61ppm).

^{13}C-NMR Spectra Showed peaks for compounds (4a,4c,4d and 4e)at the following .TheseCompounds containing C=N werecharacterized by the presence of the signals in the range of δ (152.09-159.92 ppm).The carbon signal of C=O group appeared at δ valuesbetween (163.45- 163.9 ppm),while CH3 group in these compounds appeared at δ values between(13.59-15.4 ppm).

The UV spectra of hydrazones (4a-g) Showes in chloroform as solvent intense maxima at (304-360 nm) which belonged to (π - π^*)and (n- π^*) transition.The values of IR , ^{1}H-NMR , ^{13}C-NMR and UV spectra of compounds (4a-g) are listed in table (3).

Table 3: spectral data for compounds(4a-f):

Com. No.	IR(KBr)γ Cm $^{-1}$				UV λmax (nm) $CHCl_3$	^{1} H-NMR δ(ppm) DMSO-d_6	
	C=N	C=O	CH-Ar	NH			^{13}C-NMR DMSO-d_6
4a	1616	1643	3077	3302	304	2.32(s,3H,CH_3),2.25(s,1H,OH),7.05(s,1H,NH),7.28-7.78(m,5H,ArH,acetophenone),7.18-7.58(m,1OH,ArH)	15.25,82.54,126.08,126.84,127.42,127.55,127.62,128.8,139.01,142,159.92,163.9.
4b	1616	1653	3057	3299	312	-----------------------------	---------------------------
4c	1590	1649	3060	3251	310	2.19(s,3H,CH_3),2.15(s,1H,OH),4.12(s,2H,NH_2),6.55(s,1H,NH),6.35-(d,2H,ArH,acetophenone),7.45 d,2H,ArH,acetophenone),7.22-7.61(m,1OH,ArH)	13.59,82.71,112.15,127.02,127.48,127.54,128.88,132.18,142.14,148.5,152.19,163.45.
4d	1610	1653	3022	3235	328	2.22(s,3H,CH_3),2.25(s,1H,OH),7.15(s,1H,NH),7.65d,2H,ArH,acetophenone),7.79(d,2H,ArH,acetophenone),7.237.53(m,1OH,ArH)	15.4,82.7,121.9,127.5,127.6,128.62,128.95,130.5,137.7,159.6,163.65.
4e	1597	1649	3062	3253	312	2.25(s,3H,CH_3),2.25(s,1H,OH),5.15(s,1H,OHphenolic),6.75(d,2H,ArH,acetophenone),),7.0 (s,1H,NH),7.82(d,2H,ArH,acetophenone), 7.21-7.55(m,1OH,ArH)	14.21,82.58,116.79,127.53,127,62,128.85,130.38,133.11,142.19,152.09,159.38,163.49.
4f	1581	1641	3062	3248	326	-------------------------------	------------------------
4g	1605	1654	3075	3260	360	--------------------------------------	--------------------------

While ,the IR spectrum for compounds(5a-f)showed absorbtion bands in the reagion (1618-1659cm^{-1}) stretching for (C=O amide) group , at (1585-1624 cm^{-1}) stretching group for (C=N) group , (3024-3062 cm^{-1}) and at (3232-3309cm^{-1}) due to (NH)group..The UV spectra of hydrazones (4a-g) Showes in chloroform as solvent intense maxima at (258-340 nm) which belonged to (π - π^*) an (n- π^*) transition.

In addition ,1H-NMR of compounds (5a,5 b,5d and 5e)showed significant peaks as the following .singlet at(2.15-2.35 ppm)for OH group,also siglet peak at (7.05- 7.18 ppm) due to NH gruop ,in addition the aromatic of benzophenone part showed multiplet in the range(6.38 - 7.82ppm) ,also the aromatic of part showed multiplet in the range(7.18-7.55ppm).

^{13}C-NMR Spectra Showed peaks for hydrazones (5a,5 b,5d and 5e) were found C=N groupcharacterized by the presence of the signals in the range of δ (156.42-163.65 ppm).The carbon signal of C=O group appeared at δ valuesbetween δ (163.18- 173.02 ppm),finally the carbon signal of C-OHin the range of δ (81.55 – 82.65 ppm).The values of IR , ^{1}H-NMR , ^{13}C-NMR and UV spectra of compounds (5a-f) are reported in table (4).

Table 4: spectral data for compounds(4a-f):

Com. No.	IR(KBr)γ Cm^{-1}				UV λmax (nm) $CHCl_3$	^{1} H-NMR δ(ppm) DMSO-d_6	
	C=N	C=O	CH-Ar	NH			^{13}C-NMR
5a	1597	1651	3062	3253	258	2.35(s.1H,OH),7.15(s,1H,NH),7.45-7.63(m,10H,ArH benzophenone),721-7.55(m,10H,ArH).	82.3,126.75,127.15,127.61,128.95,139,142.15,156.42,163.18
5b	1612	1651	364	3309	278	2.18(s.1H,OH),7.18(s,1H,NH),7.56-7.82(m,9H,ArH benzophenone),721-7.55(m,10H,ArH).	81.55,122.55,128.38,128.56, 128.98,131.09,138.48, 139.35,141.9,163.58,168.28
4c	1618	1649	3051	3268	338		
5d	1588	1618	3030	3256	340	2.15(s.1H,OH),3.81(s,3H,OCH_3,meta),7.15(s,1H,NH), 6.65-7.09(m,3H,ArH),7.22-7.52(m,10H,ArH),	55.4,82.54,106.5,107.8,127, 127.7,128.65,129.13,133.14,142.1,162.55,163.55,172.85
5e	1618	1649	3024	3309	294	2.18(s.1H,OH),3.65(s,3H,OCH_3),5.15(s,1H,OH),7.05(s,1H,NH), 6.38-6.98(m,3H,ArH),7.18-7.47(m,10H,ArH),7.49-7.68(m,5H,ArH1	55.7,82.65,110.8,116.7,123,126.9,127.65,128.7,131.2,133.3,142.4,154.1,173.2.
5f	1624	1659	3045	3232	304		

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