International Journal of Recent Research and Review, Vol. X, Issue 1, March 2017
ISSN 2277 – 8322

Synthesis, Characterization of Some New Benzilyl Hydrazones Derived from Benzilic Acid Hydrazide

Salim J. Mohammed, Fatin G. Zuhair
Department of Chemistry, College of Science, University of Mosul, Iraq
Email:dr_salimjasim@yahoo.com

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

***Keywords*-Benzilic acid, hydrazide, hydrazone.**

I. INTRODUCTION

It is well known that the hydrazones characterized by the presence of the tri atomic (-C=N-N-), these are distinguished from compounds by the presence of the two interlinked nitrogen atoms. Hydrazones and their derivatives show a versatile class of compounds in organic chemistry[1],these compounds have been found to possess many biological activities such as anticonvulsants[2], anti-inflammatory[3], antimalarial[4], antitumor[5], antiviral[6], antimicrobaial[7], antibacterial[8].

We have been interested in hydrazine chemistry for a long time and various axes have been explored .We found that the hydrazones are typically formed by the condensation of hydrazine or hydrazides with an aldehydes and ketones [9-10]. Thus, we have used 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.

II. EXPIMENTAL SETUP

Melting point were determined in open capillary type on Stuart melting pointSMP30.The IR spectra using KBr disk were recorded on FTIR-600 Bio Tec. Engineering Management Co.Ltd.(UK) using KBr discs.^{1}H-NMRand ^{13}C-NMR spectra were recorded on JEOLEEA400MHZFT-NMR.UV spectra were recorded on a shimadzu UV/Vis -1650 pc Spectrometer using chloroform as a solvent. The methyl benzilate (2) was prepared by the usual esterification method, benzilic acid hydrazide (3) was prepared using reported method[11]starting from methyl benzilate.

A) *Preparation of 2-Hydroxy-N-[1-substitutedphenyl)ethylidene]-2,2-diphenyl acetohydrazide[12] (4a-g)*

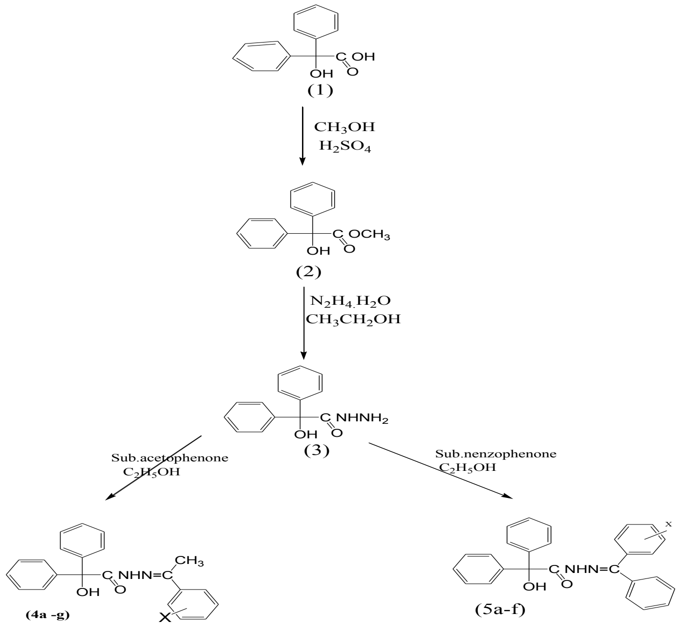
To equimolar of benzilic acid hydrazide (0.24g, 0.001mole) and substituted acetophenone (0.001mole)in absolute ethanol (30ml),(1ml) of acetic acid were added. The mixture was refluxed for six hour and then cooled in crushed ice. The solid precipitate was filtered off and recrystallized from suitable solvent. Physical and spectral data are listed in (Tables I and III).

B) *Preparation of 2-hydroxy-N-[(1- substitute dphenyl) phenyl methylene]2,2diphenyl acetohydrazide[13] (5a-f)*

A solution of benzylic acid hydrazide (0.02mole) in25 ml of ethanol was added to an ethanolic solution (25ml)of (0.02 mole) substituted benzophenone and the reaction mixture was refluxed on a water bath for 4h.,Then cooled to room temperature. The resulting solid was dried, and recrystallized from suitable solvent. Physical and spectral data are listed in (Table II and IV).

III.RESULTS AND DISCUSSION

The synthetic procedures adopted are illustrated in scheme 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.



Scheme 1

All products were characterized by physical and spectral data. The IR spectra for compounds (4a-f) showed absorption peak in the region (1643-1655 cm^{-1}) stretching for (C=O amide) group, (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_3group,(2.15-2.25ppm)for hydroxyl group, also at the range(6.55-7.15ppm) due to nh group, while the aromatic of acetophenone part showed 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 .These Compounds containing C=Newer characterized 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 values between(163.45-163.9ppm),while CH3 group in these compounds appeared at δ values between(13.59-15.4 ppm).

The UV spectra of hydrazones (4a-g) shows in chloroform as solvent intense maxima at (304-360 nm) which belonged to ($\pi - \pi^*$)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 III.

While, the IR spectrum for compounds (5a-f) showed absorption bands in the region (1618-1659cm^{-1}) stretching for (C=O amide) group , (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) Shows in chloroform as solvent intense maxima at (258-340 nm) which belonged to ($\pi - \pi^*$) 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 singlet peak at (7.05- 7.18 ppm) due to NH group. 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 for C=N group characterized 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 values between 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 IV.

IV. REFERENCES

[1] Nataliya P. Belskaya, a Wim Dehaen, b and Vasiliy A. Bakulev,ARKIVOC (i) 275-332(2010).

[2] Rahman VP, Mukhtar S, Ansari WH, Lemiere G. Eur J Med Chem.; 40: 173–184.(2005).

[3] Ito T, Fraser IP, Yeo Yoon, Highley CB, Bellas E, Kohane DS. Biomaterials; 28: 1778–1786.(2007).

[4] Acharya BN, Saraswat D, Kaushik MP. Eur J Med Chem.; 43: 2840–2852(2008).

[5] Lembege Mv.,Moreau S.,Monataudon D.,Robert J. and Nuhrich A.; Eur.J.Med.Chem.,43,1336-1343.(2008).

[6] Ossama I.,Sabbagh E., and Rady HM.Eur.J.Med.Chem.,44,3680-3686.(2009).

[7] A. Deep , S. Jain , P. C. Sharma ,P. Verma, M.Kumar and C. P. Dora,Acta Poloniae Pharmaceutica - Drug Research, Vol. 67 No. 3 pp. 255-259,(2010)

[8] F.H. Havaldar, Azadkumar S. Sharma and P. R. F. Pinto,J. Chem. Pharm. Res., 3(6):725-731,(2011).

[9] Bharat Parashar ,, P. B. Punjabi , G. D. Guptaand V. K. Sharma ;Intern.J. of Chem.Tech Research,Vol.1, No.4, pp 1022-1025,(2009).

[10] Mudrika Ahmed , F.B. Bux and Ruhi Huque,J.of Environmental Research And Development Vol. 3 No. 1,203-207,(2008).

[11] M.S.Noori,Ph.D.Thesis,Mosul university(1999).

[12] A. P. Rajputand S. S. Rajput;International J. of Pharm. and Pharma. Sci.,3(4),346-351(2011).

[13] S. R. Kelode, T. R. Kale and P. R. Mandlik;International J. of ChemTech Research,Vol.5, No.1, pp 362-366,(2013).

TABLE I

Physical constants for compounds (4a-g)

Compd. No.	Ar	Molecular Formula	M.P^{0}C	Yield %	Color	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

TABLE II

Physical constants for compounds (5a-f)

Compd. No.	Ar	Molecular Formula	M.P^{0}C	Yield %	Color	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

TABLE III
Spectral data for compounds (4a-f)

Comps. No.	IR(KBr)γ Cm $^{-1}$				UV λmax (nm) CHCl$_3$	^{1} H-NMR δ(ppm) DMSO-d$_6$	^{13}C-NMR
	C=N	C=O	CH-Ar	NH			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	2.24(s,3H,CH$_3$),2.25(s,1H,OH),7.18(s,1H,NH),7.65d,2H,ArH,acetophenone),7.77(d,2H,ArH,acetophenone),7.237.52(m,1OH,ArH)	15.44,82.7,121.9,127.5,127.6,128.62,128.95,130.5, 137.7,159.6,163.65.
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),7.45d,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	2.21(s,3H,CH$_3$),2.25(s,1H,OH),5.17(s,1H,OHphenolic),6.71(d,2H, ArH,acetophenone),),7.0 (s,1H,NH),7.80(d,2H,ArH,acetophenone), 7.24-7.52(m,1OH,ArH)	14.23,82.55,116.80,127.53,127,62,128.85,130.38,133.11,142.19,152.09,159.38,163.49.
4g	1605	1654	3075	3260	360	2.23(s,3H,CH$_3$),2.25(s,1H,OH),5.15(s,1H,OHphenolic),6.75(d,2H, ArH,acetophenone),),7.1 (s,1H,NH),7.79(d,2H,ArH,acetophenone), 7.22-7.51(m,1OH,ArH)	14.23,82.55,116.77,127.55,127,64,128.82,130.34,133.13,142.16,152.11,159.35,163.47.

TABLE IV
Spectral data for compounds (5a-f)

Comps. No.	IR(KBr)γ Cm $^{-1}$				UV λmax (nm) CHCl$_3$	^{1} H-NMR δ(ppm) DMSO-d_6	^{13}C-NMR
	C=N	C=O	CH-Ar	NH			DMSO-d_6
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
5c	1618	1649	3051	3268	338	2.19(s.1H,OH),7.17(s,1H,NH),7.56-7.81(m,9H,ArH benzophenone),720-7.53(m,10H,ArH).	81.52,122.51,128.39,128.53,128.94,131.09,138.46,139.31,141.88,163.56,168.27
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	2.16(s.1H,OH),3.68(s,3H,OCH$_3$),5.17(s,1H,OH),7.15(s,1H,NH), 6.36-6.98(m,3H,ArH),7.20-7.45(m,10H,ArH),7.48-7.65(m,5H,ArH1	55.68,82.63,110.81,116.69,123.1,126.9,127.64,128.72,131.18,133.32,142.41,154.08,173.2.