

## The Use of 3-Benzylidene Phthalide as Synthone in Synthesis of Heterocyclic Compounds

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### ABSTRACT

2-( $\alpha$ -Phenylacetyl) benzohydrazide (1) was prepared through the reaction of (Z)-3-benzylidene phthalide and hydrazine hydrate. Treatment of compound (1) with substituted benzoyl chloride yielded N'-aroyl-2-( $\alpha$ -phenyl acetyl) benzohydrazide (2a-e) which upon reaction with ammonium acetate provided the corresponding 2-phenyl-1-(2-(5-aryl-1,2,4-triazole-3-yl)phenyl)ethanones (3a-e). While the reaction of compound (1) with substituted benzaldehyde gave the hydrazones represented by N'-arylidene-2-( $\alpha$ -phenylacetyl) benzohydrazide derivatives (4a-f). Intramolecule cyclization of the latter compounds by means of acetic anhydride yielded 2-( $\alpha$ -phenylacetyl)phenyl-4-acetyl-4,5-dihydro-5-aryl-1,3,4-oxadiazoles (5a-f).

Compounds 2-( $\alpha$ -phenylacetyl)-N-(3,6-diphenyl-5-aryl-5,6-dihydro-1,2,4-triazine-4yl) benzamide (6a-f) were also obtained from the direct Diel-Alder reaction between dibenzylidene hydrazine as diene and compounds (4a-f) as dienophile enhanced by microwave irradiation.

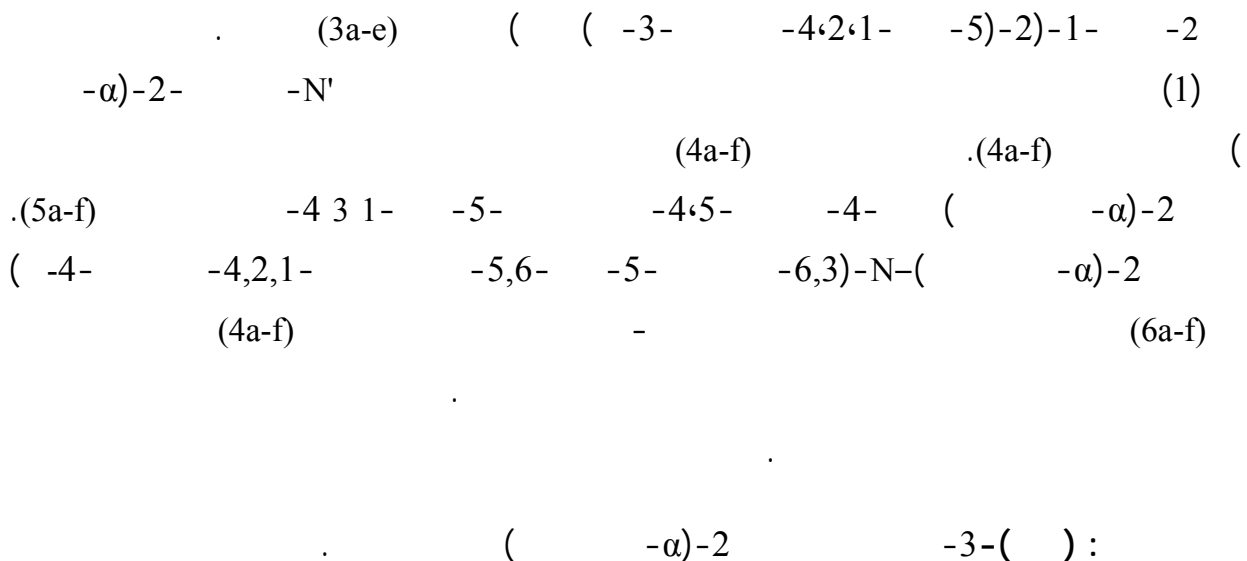
The assigned structure of the prepared compounds were corroborated by available physical and spectral methods.

**Keywords:** (Z)-3-benzylidene phthalide, 2-( $\alpha$ -phenylacetyl) benzohydrazide.

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-3-( ) (1) (  $\alpha$  )-2  
(1)  
(2a-e) (  $\alpha$  ) -2- -N'



## INTRODUCTION

Among many class of small molecule libraries, 3-benzylidene(alkylidene) phthalides are very attractive template for combinatorial synthesis, due to the large number of substitution patterns (Dalloul, 2010; Viña *et al.*, 2009; del Olmo *et al.*, 2006; Rios and Delgado, 1999; Hrnčiar *et al.*, 1994; Humber, 1974; Rosenthal and Yalpani, 1965; Litvan and Stoll, 1958) and also it have a great deals of attention because of its wide applications in industrial (Shibata and Gaesser, 1991; Scholl *et al.*, 1989; Conner, 1982) and biological fields (Kurume *et al.*, 2008; Kanazawa and Terada, 2007; Kundu *et al.*, 1998; Ganji *et al.*, 1993; Ibrahim, 1991).

In this presentation 3-benzylidene phthalide was used as active synthon to obtain different heterocyclic compounds represented by 1,2,4-triazoles that have many biological, pharmaceutical and agricultural applications (Khanage *et al.*, 2010; Singh, 2009; Taha and Al-Badry, 2006; Hsu *et al.*, 2005; Sasaki *et al.*, 1984; Katratizky and Rees, 1984), 1,3,4-oxadiazoles which present in compounds have higher biological, pharmaceutical and agricultural activities (Swamy *et al.*, 2010; mulwad and Chashar, 2006; Khare *et al.*, 2005; Mishra and Singh, 2000; Katratizky and Rees, 1984), and 1,2,4-triazines that have also reported to exhibit various pharmaceutical properties and wide applications in agricultural and industrial fields (Dalloul and Al-Shorafa, 2009; Kamble and Sudha, 2006; Nasr, 2005).

Prompted by these observations and starting from (Z)-3-benzylidene phthalide, the series of new 1,2,4-triazoles (3a-e), and 1,3,4-oxadiazoles (5a-f) were commonly performed under usual mild and thermal methods, while a simple and efficient one-pot procedure was followed for generation of 1,2,4-triazines (6a-f) with microwave assistance. The use of microwave energy to activated organic reactions has taken a new dimension in the last few years, due to its supreme properties represented by an excellent approach for the safe, rapid, environmentally safe, inexpensive and yield enhancement (Deka *et al.*, 2001; Chérouvrier and Bazureau, 2001; Xiuying *et al.*, 2003; Yan *et al.*, 2007).

### EXPERIMENTAL

Melting points (M.P.) were measured on Electrothermal, Gallenkamp melting point apparatus and are uncorrected. Proton-Nuclear Magnetic Resonance ( $^1\text{H-NMR}$ ) spectra were recorded using spectrophotometer (H300MHz); with TMS as internal standard, and  $\text{DMSO-d}_6$  as a solvent; Jordan, University of Al-Bayt. [(s) singlet; (d) doublet; (m) multiplet]. Infrared (FT-IR) spectra were recorded as (KBr) disc using a Bruker, FT-IR, spectrophotometer tensor 27 and FT-IR-600, Biotech Engineering Mangment CO. LTD. (UK). Ultraviolet (UV) spectra were performed on Shimadzu UV-Visible spectrophotometer UV-1650 PC using methanol as a solvent. The microwave oven is a domestic microwave oven (LG, MS-192W), (360watt) irradiation was used. The starting material (Z)-3-benzylidene phthalide was manufactured by Fluka Com. (Germany). Finally, thin layer chromatography (T.L.C) were carried out on silica gel (120 mesh) coated plates (2x10) cm, one hour activated at (110-120°C) before use .

#### **Synthesis of 2-( $\alpha$ -phenylacetyl) benzohydrazide (1): (Del Olmo *et al.*, 2006, 2010; Shafiee *et al.*, 1995)**

To a solution of (Z)-3-benzylidene phthalide (2.22 gm, 1 mmole) in ethanol (25 ml), hydrazine hydrate (80%) (2.5 gm, 0.05 mole) was added dropwise. The resulting mixture was vigorously stirred for (5 hrs.), then poured on (100 ml) ice-water. The white precipitate was filtered off and washed thoroughly with water and crystallized from ethanol to give (1.7 gm, 73%) of compound (1); m.p (195-196°C); The purity of the obtained product was controlled by TLC technique using solvent system (ethyl acetate:dichloromethane) in (2:8) ratio,  $R_f$  value (0.330);  $^1\text{H-NMR}$  ( $\text{DMSO-d}_6$ )  $\delta$ /ppm: 3.4(1H, $\text{NH}_2$ ), 4.3(2H, $\text{CH}_2$ ), 7.1-8.2(H-Ar) and 12,4(1H, $\text{NH}$ ); FT-IR (KBr)  $\nu/\text{cm}^{-1}$ : 3340( $\text{NH}_2$ ), 3161( $\text{NH}$ ), 1692( $\text{C=O}$  ketone), 1660( $\text{C=O}$  amide), and 1076 (N-N); UV (methanol,  $\lambda_{\text{max}}$ ): 242 nm.

#### **Synthesis of N'-aroyl-2-( $\alpha$ -phenylacetyl) benzohydrazide (2a-e): (Patel *et al.*, 2010; Sobkowski, 2008; Trotsko *et al.*, 2007)**

Substituted benzoyl chloride (5 mmole) was added to a stirred solution of compound (1) (1.2 gm, 5 mmole) in pyridine (10 ml) and catalytic amount of triethylamine (1 ml). The mixture was stirred for (20) minutes at room temperature, then refluxed for (2 hrs.). The reaction mixture was brought to room temperature and left overnight. The precipitated solid was filtered off, washed with ether (3x15 ml), and dried then recrystallized from ethanol to yield compounds (2a-e). The completion of the reaction was monitored by thin layer chromatography (TLC) and the physical and spectral data were shown in Table (1).

Table 1: Physical properties and spectral data for compounds (2a-e).

Comp. No.	X	M.P. (°C)	Yield (%)	R <sub>f</sub> Value	UV (MeOH) λ <sub>max</sub> (nm)	I.R (KBr) ν (cm <sup>-1</sup> )					
						N-H	C=O (ketone)	C=O (amide)	C=C (Ar)	N-N	others
2a	H	238-240	95	0.26	226	3203	1709	1664	1601,1475	1076	—
2b	p- Cl	174-177	94	0.23	236	3222	1736	1682	1600,1493	1092	—
2c	2,4-di Cl	243-244	91	0.21	232	3184	1720	1687	1609,1475	1078	—
2d	p-NO <sub>2</sub>	152-154	72	0.22	232	3159	1712	1658	1604,1477	1076	NO <sub>2</sub> asym 1523 sym 1358
2e	3,5-di NO <sub>2</sub>	240-242	74	0.25	232	3232	1720	1658	1608,1475	1072	NO <sub>2</sub> asym 1535; sym 1331

### Synthesis of 2-phenyl-1-(2-(5-aryl-1,2,4-triazole-3-yl)phenyl)ethanones (3a-e): (Konda, 2010, Abd El-Fattah et al., 2010; Nasr, 2005)

A mixture of compounds (2a-e) (0.3 mmole) and ammonium acetate (0.6 mmole) in methanol (25 ml) was heated under reflux for (5 hrs.), then left to cool to room temperature. The reaction mixture was poured into cold water for complete precipitation, then the solid obtained was filtered off, washed with ether (2x5 ml). The crude product was crystallized from methanol to give compounds (3a-e). The completion of the reaction was monitored by thin layer chromatography (TLC) (ethyl acetate: dichloro methane, 2:8 ratio) and the physical and spectral data were shown in Table (2).

Table 2: Physical properties and spectral data for compounds (3a-e).

Comp. No.	X	M.P. (°C)	Yield (%)	R <sub>f</sub> Value	UV (MeOH) λ <sub>max</sub> (nm)	I.R (KBr) ν (cm <sup>-1</sup> )					
						N-H	C=O	C=C (Ar)	C=N (cyclic)	N-N	others
3a	H	215-218	82	0.50	268	3180	1668	1603,1481	1631	1078	—
3b	p- Cl	192-194	92	0.45	268	3200	1682	1604,1479	1591	1092	—
3c	2,4-di Cl	221-223	75	0.35	264	3159	1665	1616,1475	1575	1072	—
3d	p-NO <sub>2</sub>	190-192	82	0.37	256	3244	1658	1608,1493	1554	1076	NO <sub>2</sub> asym 1554 sym 1338
3e	3,5-di NO <sub>2</sub>	218-220	65	0.31	276	3140	1662	1611,1479	1572	1072	NO <sub>2</sub> asym 1533; sym 1365

**Synthesis of N'-arylidene-2-( $\alpha$ -phenylacetyl)benzohydrazide (4a-f): (Kotb, 2009)**

A mixture of compound (1) (2.36 gm, 10 mmole) and equimolar amount of the substituted benzaldehyde in absolute ethanol (20 ml) was refluxed for (8 hrs.). The solution was cooled, the precipitate formed was filtered off and recrystallized from methanol to give compounds (4a-f). The completion of reaction was followed by TLC (ethyl acetate: dichloro methane, 2:8 ratio). The physical and spectral data were listed in Table (3).

Table 3: Physical properties and spectral data for compounds (4a-f).

Comp. No.	X	M.P. (°C)	Yield (%)	R <sub>f</sub> Value	UV (MeOH) $\lambda_{\max}$ (nm)	I.R (KBr) $\nu$ (cm <sup>-1</sup> )						
						N-H	C=O (ketone)	C=O (amide)	C=C (Ar)	C=N	N-N=C	others
4a	H	172-174	73	0.53	284	3180	1728	1661	1601,1493	1560	1542	—
4b	p-OMe	155-156	69	0.47	328	3161	1704	1658	1600,1493	1563	1547	acyclic C-O-C, 1181
4c	2,4-diOMe	176-177	61	0.39	352	3165	1720	1658	1603,1493	1580	1549	acyclic C-O-C, 1181
4d	3,4-diOMe	177-179	65	0.42	304	3223	1711	1655	1602,1508	1597	1579	acyclic C-O-C, 1188
4e	o-Cl	138-139	84	0.38	344	3239	1727	1655	1608,1491	1587	1564	—
4f	p-Cl	174-175	90	0.45	308	3211	1720	1657	1608,1491	1593	1558	—

**Synthesis of 2-( $\alpha$ -phenyl acetyl)phenyl-4-acetyl-4,5-dihydro-5-aryl-1,3,4-oxadiazole (5a-f): (Kotb, 2009; Islam and Mohsin, 2007; Shaban *et al.*, 1991 )**

A mixture of compounds (4a-f) (0.5 mmole) and acetic anhydride (7 ml) were refluxed for (3 hrs.). The excess of acetic anhydride and acetic acid were removed in vacuo and the solid residue was filtered off, washed with water, dried and recrystallized from ethanol to give the compounds (5a-f). The completion of reaction was followed by TLC (ethyl acetate: dichloro methane, 2:8 ratio). The physical and spectral data were given in Table (4).

Table 4: Physical properties and spectral data for compounds (5a-f)

Comp. No.	X	M.P. (°C)	Yield (%)	R <sub>f</sub> Value	UV (MeOH) $\lambda_{\max}$ (nm)	I.R (KBr) $\nu$ (cm <sup>-1</sup> )					
						C=O (ketone)	C=O (amide)	C=C (Ar)	C=N	C-O-C (cyclic)	others
5a	H	96-97	69	0.45	232	1759	1674	1608,1495	1597	1190	—
5b	p-OMe	88-89	95	0.41	234	1759	1672	1610,1495	1597	1190	acyclic C-O-C, 1126
5c	2,4-diOMe	92-94	85	0.36	236	1755	1668	1600,1493	1597	1190	acyclic C-O-C, 1124
5d	3,4-diOMe	157-160	90	0.38	232	1759	1660	1600,1493	1597	1182	acyclic C-O-C, 1153
5e	o-Cl	94-95	84	0.43	236	1751	1672	1601,1495	1558	1163	—
5f	p-Cl	170-171	89	0.40	250	1709	1650	1616,1491	1591	1180	—

#### Synthesis of 2-( $\alpha$ -phenylacetyl)-N-(3,6-diphenyl-5-aryl-5,6-dihydro-1,2,4-triazine-4-yl) benzamide (6a-f): (Lenardao *et al.*, 2007)

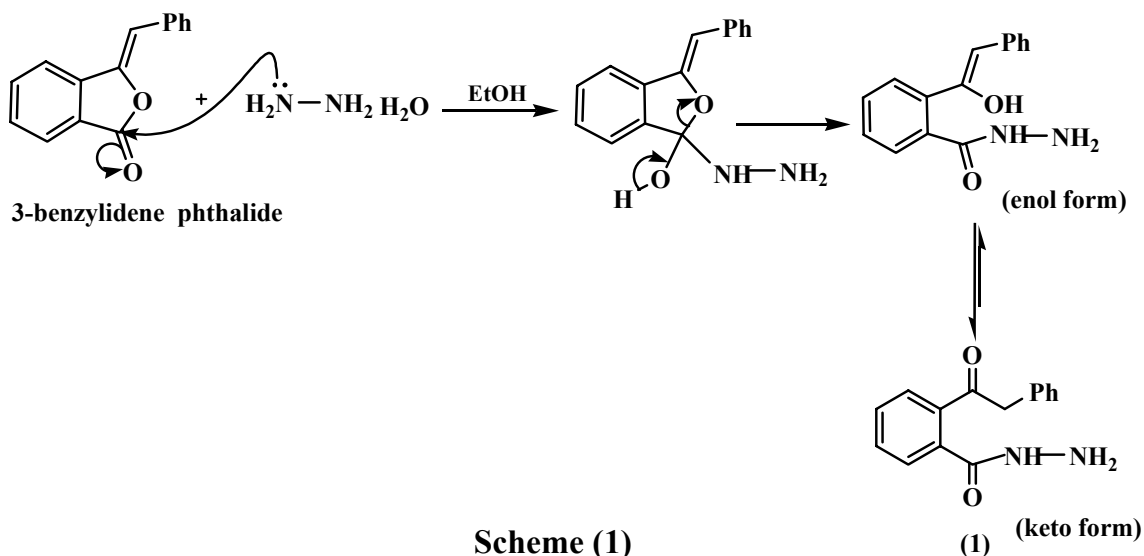
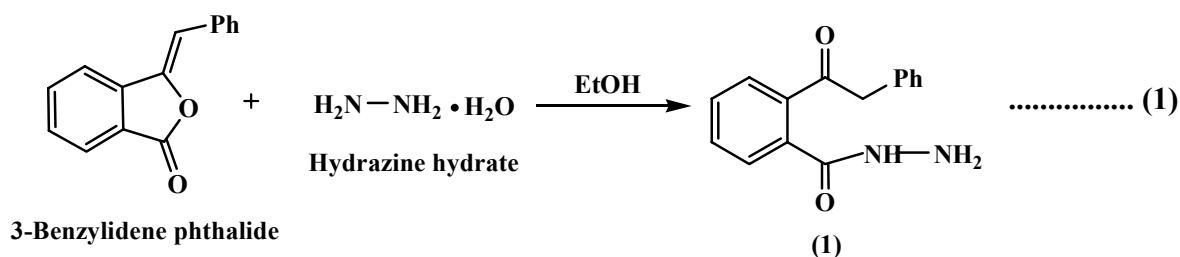
Equimolar of compounds (4a-f) and dibenzylidene hydrazine (which was prepared using a previously reported method, Sharma *et al.*, 2008) were irradiated in a microwave oven for (6 min.) at (360 watt). After cooling, cold water was added to the reaction mixture, the solid obtained was then filtered off and recrystallized from ethanol. The completion of reaction was followed by TLC (ethyl acetate: dichloro methane, 2:8 ratio). The physical and spectral data were listed in Tables (5).

Table 5: Physical properties and spectral data for compounds (6a-f)

Comp. No.	X	M.P. (°C)	Yield (%)	R <sub>f</sub> Value	UV (MeOH) $\lambda_{\max}$ (nm)	I.R (KBr) $\nu$ (cm <sup>-1</sup> )							
						N-H	C=O (ketone)	C=O (amide)	C=C (Ar)	N=N	C-N	N-N	others
6a	H	120-121	85	0.49	298	3356	1733	1656	1625,1493	1577	1348	1075	—
6b	p-OMe	110-112	74	0.36	300	3328	1750	1656	1625,1492	1556	1378	1074	acyclic C-O-C 1151
6c	2,4-diOMe	130-132	69	0.31	298	3340	1713	1656	1622,1493	1589	1348	1076	acyclic C-O-C 1152
6d	3,4-diOMe	119-120	69	0.33	300	3289	1718	1655	1622,1492	1574	1346	1074	acyclic C-O-C 1152
6e	o-Cl	116-118	98	0.45	304	3290	1714	1657	1618,1491	1591	1354	1084	—
6f	p-Cl	120-122	83	0.42	298	3300	1739	1655	1622,1491	1593	1354	1076	—

## RESULTS AND DISCUSSION

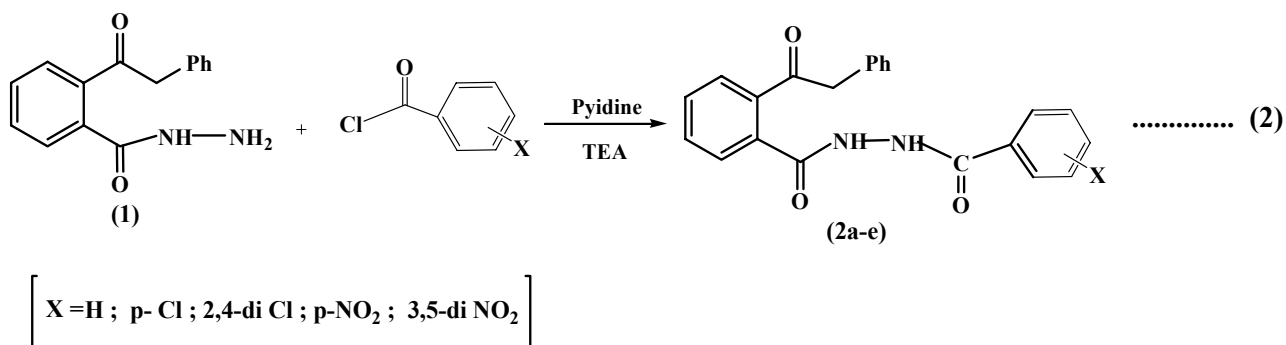
The synthetic pathway leading to the title compounds is given in scheme (7). Usually, the key intermediate 2-( $\alpha$ -phenyl acetyl) benzohydrazide (1) was achieved by stirring the (*Z*)-3-benzylidene phthalide and hydrazine hydrate (80%) in ethanol according to the previously described procedure (equation 1). Scheme (1) summarized the mechanism probably proceeded for this reaction, (Chiriac *et al.*, 2007; Youssef, 2006) .



Scheme (1)

The structure of compound (1) was established on the bases of spectral data. Thus, its IR spectrum displays appearance of absorption bands at ( $3340\text{ cm}^{-1}$ ), ( $3161\text{ cm}^{-1}$ ), ( $1692\text{ cm}^{-1}$ ), ( $1658\text{ cm}^{-1}$ ) and ( $1076\text{ cm}^{-1}$ ) due to  $\text{NH}_2$ ,  $\text{NH}$ ,  $\text{C}=\text{O}$  (ketone) and  $\text{C}=\text{O}$  (amide) and  $\text{N}-\text{N}$  functional groups respectively. While, the UV spectrum showed absorption band at  $\lambda_{\text{max}}$  (242 nm) due to the  $n \rightarrow \pi^*$  transition (Finar, 1977; Parkh, 1974). Further structure proof of compound (1) has come from  $^1\text{H-NMR}$  spectrum which showed significant peaks at  $\delta$  (ppm): 3.4 (s, 2H,  $\text{NH}_2$ ), 4.3 (s, 2H,  $\text{CH}_2$ ), 7.1-8.2 (m, H-aromatic) and 12.6 (s, 1H,  $\text{NH}$ ).

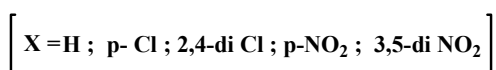
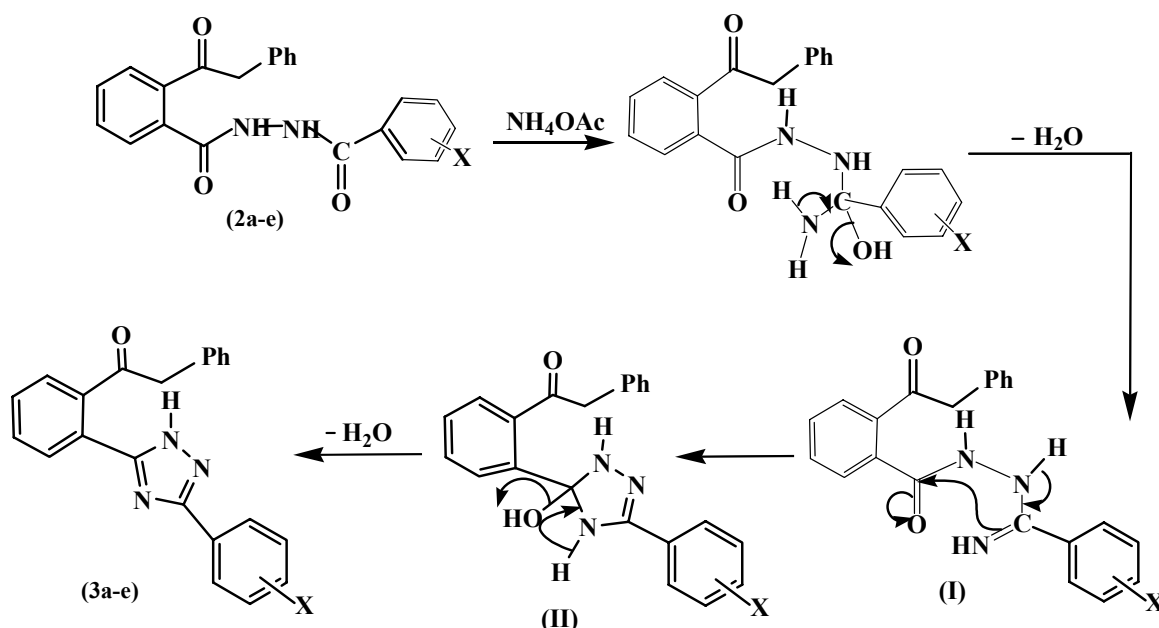
Treatment of compounds (1) with substituted benzoyl chloride in pyridine and catalytic amounts of triethylamine afforded the N'-aroyl-2-( $\alpha$ -phenyl acetyl) benzohydrazide derivatives (2a-e) in good yields as shown in equation (2), (Ferwanah and Awadallah, 2005; Yildirim *et al.*, 2005; Demirbas *et al.*, 2005).



The structure of these compounds was confirmed by means of IR and UV spectra, Table (1). The IR spectra show the characteristic N-H, C=O(ketone), C=O(amide), C=C(aromatic) and N-N absorption bands appeared at ( $3159\text{-}3222\text{ cm}^{-1}$ ), ( $1709\text{-}1736\text{ cm}^{-1}$ ), ( $1658\text{-}1687\text{ cm}^{-1}$ ), ( $1600\text{-}1609$ ;  $1475\text{-}1493\text{ cm}^{-1}$ ) and ( $1072\text{-}1092\text{ cm}^{-1}$ ) respectively and the band at ( $3379\text{ cm}^{-1}$ ) which assigned to  $\text{NH}_2$  functional group in compound(1) was disappeared. The absence of this band indicates the conversion of the  $\text{NH}_2$  group in to NH amido group. Also, the UV spectra of these compounds showed decreases in the absorption wavelength at  $\lambda_{\text{max}}$  ( $220\text{-}236\text{ nm}$ ) compared with those for compound (1), (Finar, 1977). On the other hand, the structure of compound (2a) as a representative example, was confirmed by  $^1\text{H-NMR}$  spectra which shows significant peaks at  $\delta$  (ppm): 3.4 (s,2H, $\text{CH}_2$ ), 7.5-7.9 (m,H-aromatic) and 10.5-10.6 (d,2H,NH).

Reaction of compounds (2a-e) with ammonium acetate yielded the corresponding 2-phenyl-1-(2-(5-aryl-1,2,4-triazole-3-yl)phenyl)ethanone derivatives (3a-e). Mechanistically, it is reasonable to assume that the ammonium acetate was decomposed under reflux conditions to releases ammonia and acetic acid (Konda *et al.*,2010; Bangar *et al.*, 2008; Adib *et al.*,2006; Rao and Senthilkumar, 2004). Dehydrative condensation of ammonia and C=O (amido) of compounds (2a-e) provides the intermediate (I). Subsequently, this intermediate undergoes intramolecule cyclization involving the other C=O (amido) group to give compounds (3a-e) as shown in scheme (2) ( Youssef, 2006).



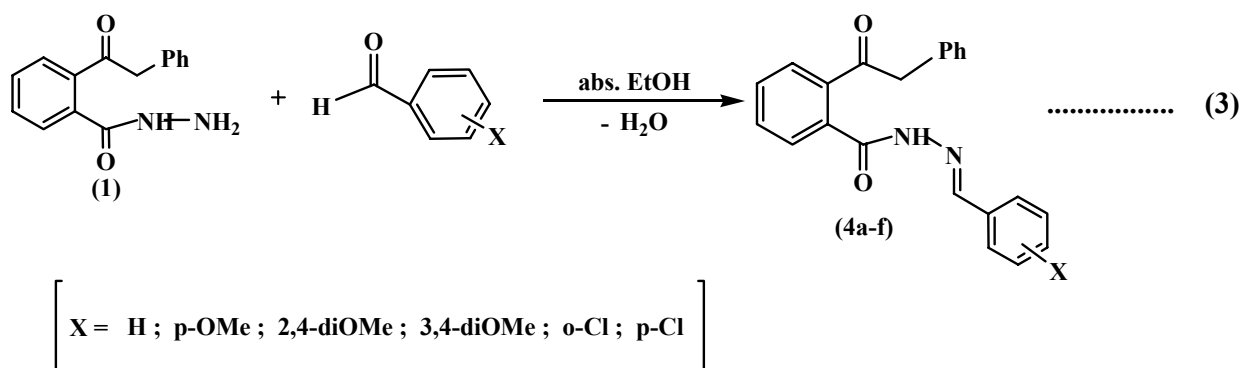


Scheme (2)

The NH, C=O (ketone), C=C (aromatic), C=N (cyclic) and N-N bonds stretching in IR spectra of the latter compounds appeared at ( $3140\text{-}3244\text{ cm}^{-1}$ ), ( $1658\text{-}1682\text{ cm}^{-1}$ ), ( $1603\text{-}1611$ ;  $1475\text{-}1493\text{ cm}^{-1}$ ), ( $1554\text{-}1631\text{ cm}^{-1}$ ) and ( $1072\text{-}1092\text{ cm}^{-1}$ ) respectively, Table (2). Furthermore, in UV spectra these compounds showed a maximum absorption at  $\lambda_{\text{max}}$  (256-276 nm), this reasing in absorption is attributed to the formation of 1,2,4-triazole ring (Lopyrev *et al.*, 1977). The  $^1\text{H-NMR}$  measurement of compound (3b) showed the following characteristic peaks at  $\delta$  (ppm): 2.9 (s,2H,CH<sub>2</sub>), 7.2-7.9 (m,H-aromatic) and 13.2 (s,1H,NH).

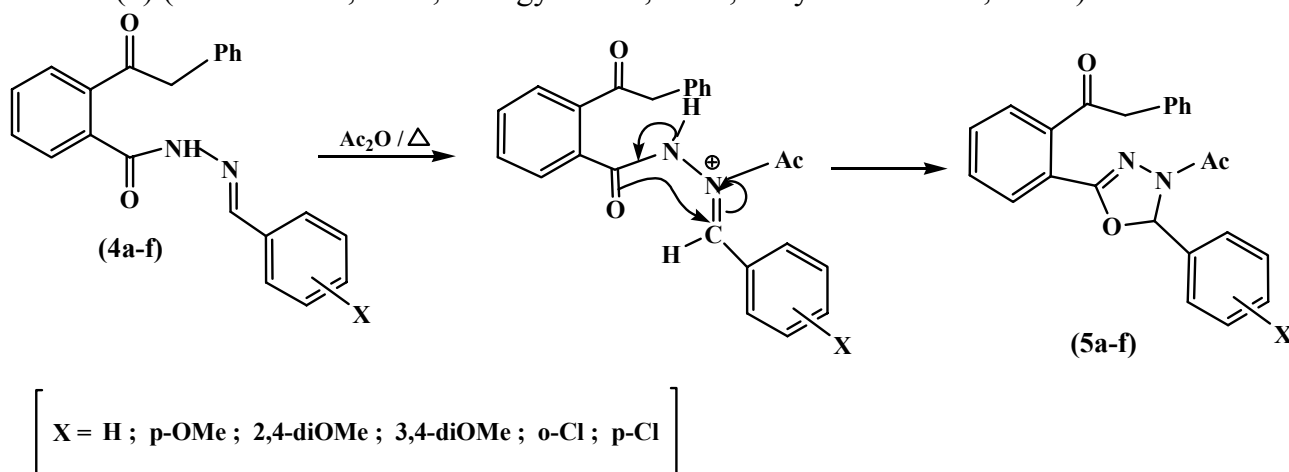
The purity of the synthesized compounds were checked by thin layer chromatography measurements, and this technique was also used to established the formation of compounds (3a-e) by comparing their R<sub>f</sub> values with those of compounds (2a-e) as listed in Tables (1 and 2) respectively.

Condensation of compounds (1) with substituted benzaldehyde was found to proceed concurrently to equation (3) (Kotb *et al.*, 2009; Hsu *et al.*, 2005; Cid *et al.*, 2000) to give the corresponding N'-arylidene-2-( $\alpha$ -phenylacetyl)benzohydrazide derivatives (4a-f).



The structure of these compounds was confirmed from their spectral data, Table (3). Thus, the IR spectra of these compounds showed the following spectral bands: NH functional group at ( $3161\text{-}3231\text{ cm}^{-1}$ ), ( $1704\text{-}1728\text{ cm}^{-1}$ ) and ( $1655\text{-}1661\text{ cm}^{-1}$ ) related to the C=O groups (ketone and amide) respectively (Çakır and Biçer, 2010) and ( $1600\text{-}1608$ ;  $1491\text{-}1508\text{ cm}^{-1}$ ) related to C=C (aromatic). In contrast, the appearance of the C=N bond stretching at ( $1560\text{-}1597\text{ cm}^{-1}$ ) and N=N=C bond stretching at ( $1542\text{-}1579\text{ cm}^{-1}$ ) (Valentina *et al.*, 2009; Solak and Rollas, 2006) gave an evidence for the formation of compounds (4a-f). Whereas, in UV spectra they gave assigned absorption bands at  $\lambda_{\text{max}}$  ( $284\text{-}352\text{ nm}$ ) due to the imine  $\pi \rightarrow \pi^*$  transition (Hadi *et al.*, 2009). The structure of compound (4e) was further identified by  $^1\text{H-NMR}$  spectrum, it showed a significant absorption peaks at  $\delta$  (ppm): 3.4 (s, 2H, CH<sub>2</sub>), 4.3 (s, 1H, CH=N), 7.1-8.9 (m, H-aromatic) and 12.7 (s, 1H, NH).

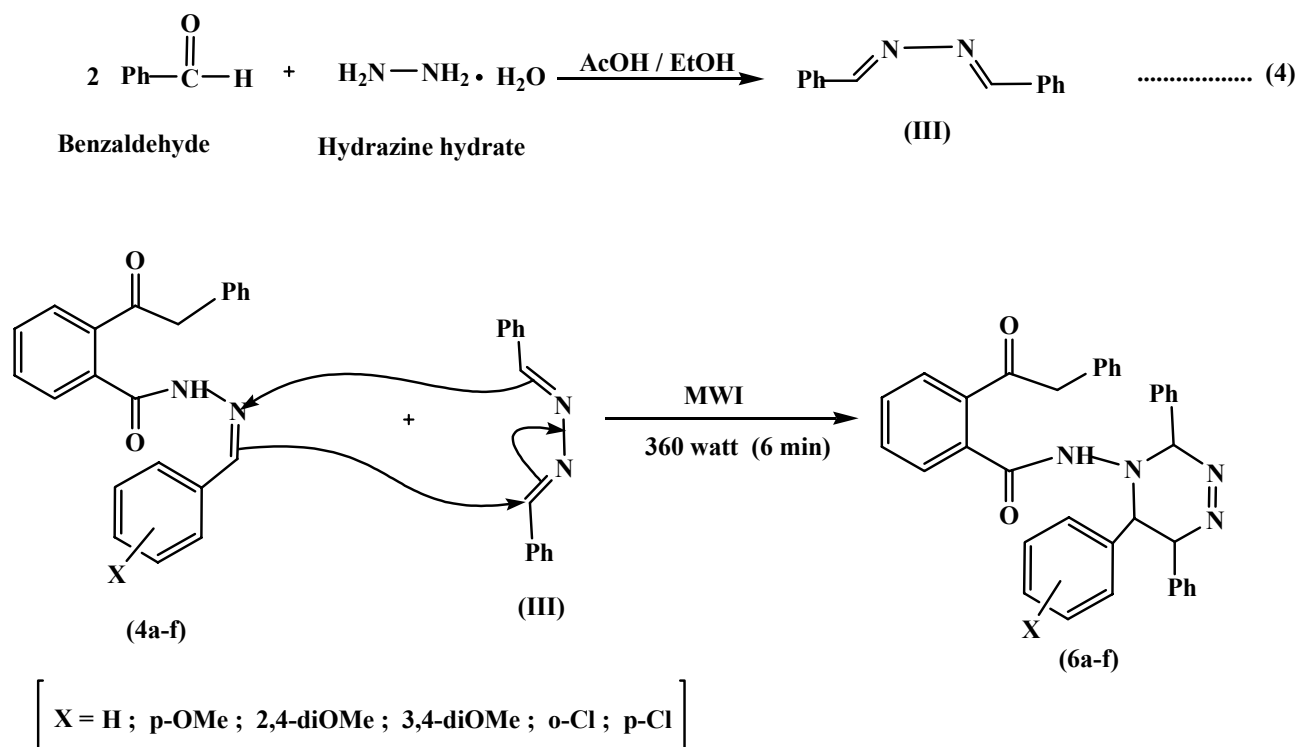
Compounds (4a-f) can be considered as useful intermediate leading to formation several Heterocyclic compounds. Thus, the ring closure reaction of compounds (4a-f) in presence of excess acetic anhydride under reflux condition for (4hrs.) gave the corresponding 2-(2-phenylacetyl)phenyl-4-acetyl-4,5-dihydro-5-aryl-1,3,4-oxadiazoles (5a-f) as shown in the following scheme (3) (Fuloria *et al.*, 2009; Szilágyi *et al.*, 2004; Boyd and Dando, 1971).



Scheme (3)

In each case, IR and UV spectra of the isolated products completely agree with the suggested structure, Table 4. The IR spectra show a characteristic bands at (1163-1190 $\text{cm}^{-1}$ ) (1600-1616;1491-1495 $\text{cm}^{-1}$ ), (1558-1597 $\text{cm}^{-1}$ ), (1650-1674 $\text{cm}^{-1}$ ) and (1709-1759 $\text{cm}^{-1}$ ) related to C-O-C (cyclic), C=C (aromatic), C=N, C=O (amide) (Islam and Mohsin, 2007) and C=O (ketone) bonds stretching respectively. The UV spectra, on the other hand showed blue shift with maximum absorption at  $\lambda_{\text{max}}$  (232-250 nm) which assigned to the formation of 1,3,4-oxadiazoline ring (Kudelko and Zieliński, 2009), this provided additional evidence for the formation of compounds (5a-f). On the other hand, the  $^1\text{H-NMR}$  measurement of compound (5f) as a representative example showed the following characteristic peaks at  $\delta(\text{ppm})$ : 2.4 (s,3H, $\text{CH}_3$ ), 3.4 (s,2H, $\text{CH}_2$ ), 6.7 (s,1H, $\text{CH-oxadiazoline}$ ) and 7.2-8.5 (m,H-aromatic).

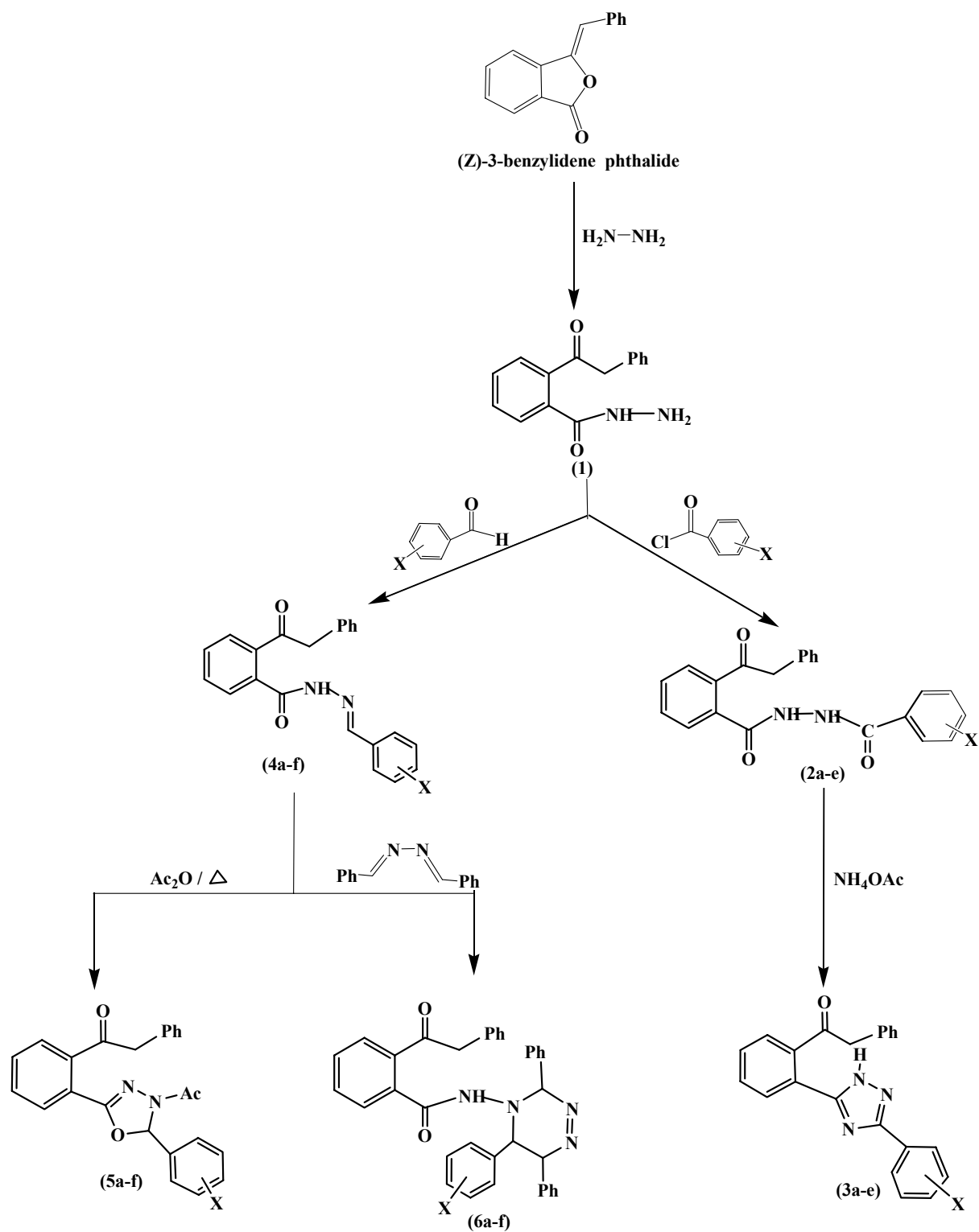
It is also worth noting that compounds 2-( $\alpha$ -phenylacetyl)-N-(3,6-diphenyl-5-aryl-5,6-dihydro-1,2,4-triazine-4yl)benzamide (6a-f) were prepared through direct Diels-Alder reaction between dibenzylidene hydrazine (III) as diene (was prepared by condensation of hydrazine hydrate (80%) with benzaldehyde in the presence of aqueous acetic acid (50%) to give yellowish green crystalline products in a good yield (Sharma *et al.*, 2008) as shown in scheme (4), equation 4) and compounds (4a-f) as dienophile. The reaction was found to proceed smoothly under microwave irradiation within (6 min.) at (360 watt), (scheme 4) (Carey,1996).



Scheme (4)

The products were elucidated from their spectral analysis, Table (5). The IR spectra they show absorption bands at (3289-3356  $\text{cm}^{-1}$ ) related to NH functional group, (1713-1750  $\text{cm}^{-1}$ ) assigned to C=O (ketone) functional group, (1655-1657  $\text{cm}^{-1}$ ) assigned to C=O (amide) functional group, (1618-1625; 1491-1493  $\text{cm}^{-1}$ ) related to C=C (aromatic), (1556-1593  $\text{cm}^{-1}$ ) assigned to N=N functional group, (1346-1378  $\text{cm}^{-1}$ ) assigned to C-N functional group and at (1074-1084  $\text{cm}^{-1}$ ) assigned to N-N functional group. The absence of C=N absorption band and the presence of N=N absorption bands indicate clearly the formation of compounds (6a-f). Also, these compounds have UV absorption between (298-304 nm) comparing with those for compounds (4a-f). Further identification of compound (6e) has come from  $^1\text{H}$ -NMR measurement, which showed significant peaks at  $\delta$  (ppm): 2.4 (s, 1H, CH), 2.6 (s, 1H, CH), 3.3 (s, 2H,  $\text{CH}_2$ ), 4.3 (s, 1H, CH) and 7.1-8.9 (m, H-aromatic) and 12.7 (s, 1H, NH).

Finally, ethyl acetate: dichlor methane, was used as suitable solvent system in thin layer chromatography measurements to give an indication about the formation of compounds (5a-f) and (6a-f) and also comparing their  $R_f$  values with those of the starting materials represented by compounds (4a-f) as shown in Tables (5,4 and 3) respectively.



Scheme (5)

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