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A New Method for the Synthesis of Some 1,5-Diphenyl-3- Aryl-4,5-Dihydro-1,2,4-Triazole

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ABSTRACT

Condensation of aromatic aldehydes with benzamide affords the corresponding arylidenbenzamide as a new conjugated system . The reaction between these compounds and phenylhydrazine in acidic medium gives the corresponding triazoles.

The new synthesised compounds are characterized by using physical and spectrometric methods .

طريقة جديدة لتحضير بعض مركبات- 5,1- ثنائي فنيل-3- أريل-5,4- ثنائي هايدرو-4,2,1-ترايازول

الملخص

تتكاثف ألالديهايدات ألأروماتية مع البنزامايد لتعطي مركبات الأريليدين بنزامايد والتي تعتبر من الانظمة المتعاقبة الجديدة (1-10). إن التفاعل مابين هذه المركبات مع الفنيل هيدرازين في الوسط الحامضي يؤدي الى إعطاء مركبات الترايازول (11-20). تم إثبات الصيغ التركيبية للمركبات المحضرة بأستخدام الطرق الفيزيائية والطيفية.

INTRODUCTION

α ,β-Unsaturated carbonyl compounds are considered to be an important structural unit to built alarge number of organic compounds especially heterocyclic compounds (Saied, 2000; Said, 1998, Marzinzik and Felder, 1998). This importance will be greter by replacing the α-carbon atom by a hetero atom such as nitrogen,thus from this point a new conjugated system has been synthesised represented by arylidenebenzamide (1-10) which inturn used in the synthesis of substituted 1,2,4-Triazoles (11-20) as a heterocyclic compounds. 1,2,4-Triazoles and their derivatives like all heterocyclic compounds possess a wide spectrum of activities and applications, they represent one of the most biologically active classes of compounds, and it′s nucleus is associated with diverse pharmacological activities such as analgesic (Mekuskien et al., 1998), antibacterial (Ragenovic et al., 2001), antifungal (Salama et al., 2001), antiinflamatory (Sahin et al., 2001), antimicrobial

(Zamani et al., 2004), antimycotic (Wujec et al., 2004) and antitumer actions (Demirbas and Ugurluoglu, 2004). Furthermore,1,2,4-triazoles have applications in other fields such as industry as plastics stabilizers (Mingawa et al., 1973) and corrosion inhibitors (Khamis and Atea, 1994). So in the present study, promoted by these observations, the synthesis of a series of 1,2,4-triazoles are performed .

EXEPRIMENLAL

Melting points were measured on Electrothermal 9300 melting point apparatus and are uncorrected. IR spectra were recorded in KBr disc using a Bruker, FT-IR, spectrophotometer tensor 27. UV spectra were performed on Shimadzu UV-Visible spectrophotometer UV-1650 PC using methanol as a solvent.

Synthesis of Arylidenebenzamide (1-10)

These compounds have been synthesised by the following two methods:

Method (A): (Vogel, 1981)

To a solution of aromatic aldehyde (0.02 mole) in (30 mL) of methanol (99.5٪), benzamide (0.02 mole, 2.42 gm) was added. The reaction mixture was refluxed for (24 hours), the solvent then was evaporated under vaccum and the solid was collected and recrystallised from xylene .

Method (B): (Fieser and Fieser, 1975)

Amixture of aromatic aldehyde (0.02 mole), triethylamine (3 mL) and benzamide (0.02 mole, 2.42 gm) in (30 mL) of benzene was refluxed for (24 hours) the solvent then was evaporated under vaccum and the solid was collected, washed with petroleum ether (60-80) and recrystallised from xylene. The physical and spectral data for these compounds are recorded in Table (1) .

Table 1: Physical and spectral data for compounds(1-10)

Compd .no.	X	Molecular formula	M.P. (C°)	Yield (%)	UV(MeOH) λ max (nm)	IR(KBr) v	
						C=O	C=N
1	H	$C_{14}H_{11}NO$	113-115	61	282	1653	1577
2	4-Cl	$C_{14}H_{10}ClNO$	122-125	21	283	1658	1577
3	4-OMe	$C_{15}H_{13}NO_2$	124-125	42	283	1651	1575
4	2-Cl	$C_{14}H_{10}ClNO$	115-118	31	282	1654	1577
5	2,6-di-Cl	$C_{14}H_9Cl_2NO$	123-125	34	282	1659	1577
6	3,4-di-OMe	$C_{16}H_{15}NO_3$	125-126	37	283	1651	1575
7	2,3-di-OMe	$C_{16}H_{15}NO_3$	121-123	39	283	1651	1578
8	2,4-di-OMe	$C_{16}H_{15}NO_3$	125-127	37	283	1651	1578
9	2-OH	$C_{14}H_{11}NO_2$	125-128	49	283	1662	1577
10	3-NO_2	$C_{14}H_{10}N_2O_3$	123-126	42	284	1660	1578

Synthesis of 1,5 - di phenyl - 3 – Aryl - 4,5 - di hydro -1,2,4 - triazoles (11-20):

A mixture of (0.5 gm) of the compounds (1-10) and phenylhydrazine (0.0046 mole,0.5 gm) in (30 mL) of glacial acetic acid was refluxed for (3 hours). After cooling the mixture to room temperature, the solution was diluted with cold water. The precipitate formed was collected by filtration, washed with cold water and recrystallised from carbon tetrachloride. (Joshi and Jauhar, 1965).

If the product doesn't precipitate directly in water, it will be extracted in benzene (3×30 mL), the benzene layer is seperated, dried with magnesium sulfate, filtered and evaporated under vaccum. The precipitate that formed was collected and recrystallised from carbon tetrachloride.The physical and spectral data for these compounds are recorded in table (2).

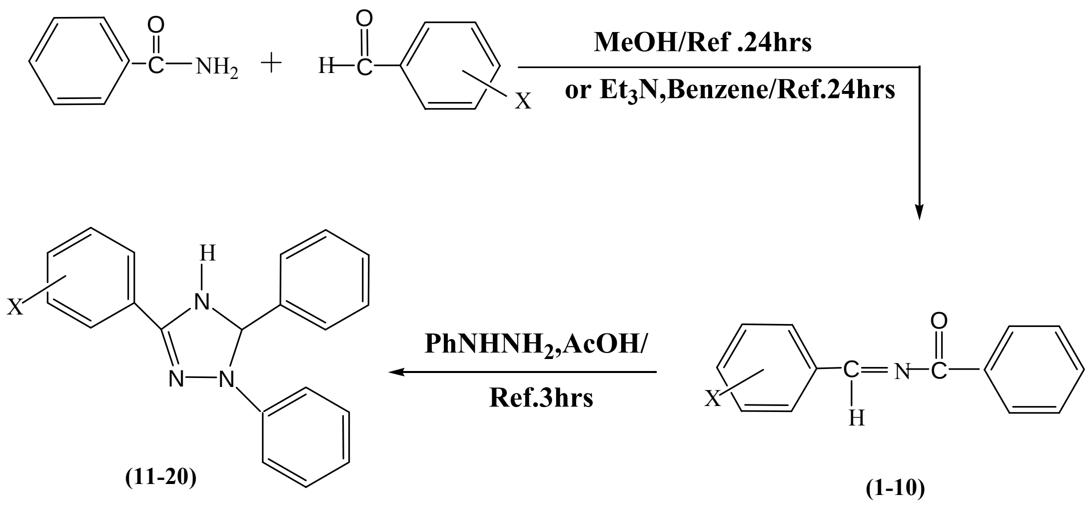
Table 2: Physical and spectral data for compounds(11-20)

Compd.no.	**X**	**Molecular formula**	**M.P. (C°)**	**Yield(%)**	**UV(MeOH) λ max (nm)**	**IR (KBr)**	
						N — H	**C = N**
11	H	$C_{20}H_{17}N_3$	147-149*	60	300	3423	1566
12	4-Cl	$C_{20}H_{16}ClN_3$	99-101	65	292	3428	1575
13	4-OMe	$C_{21}H_{19}N_3O$	97-99	51	289	3428	1576
14	2-Cl	$C_{20}H_{16}ClN_3$	100-103	59	289	3428	1574
15	2,6-diCl	$C_{20}H_{15}Cl_2N_3$	104-106	91	292	3427	1574
16	3,4-di-OMe	$C_{22}H_{21}N_3O_2$	99-100	69	294	3427	1575
17	2,3-di-OMe	$C_{22}H_{21}N_3O_2$	88-90	46	286	3421	1576
18	2,4-di-OMe	$C_{22}H_{21}N_3O_2$	98-101	98	295	3421	1578
19	2-OH	$C_{20}H_{17}N_3O$	98-100	43	290	3428	1574
20	3-NO_2	$C_{20}H_{16}N_4O_2$	97-99	59	290	3422	1576

(★)Recorded 141-142°(Huisgen et al.,1965)

RESULTS AND DISCUSSION

In this work, it's obviously that the method that applied in the synthesis of some substituted 1,2,4-triazoles (11-20) has never been used before, which involve the reaction between arylidenebenzamide (1-10) and phenylhydrazine in presence of glacial acetic acid (Scheme 1) .

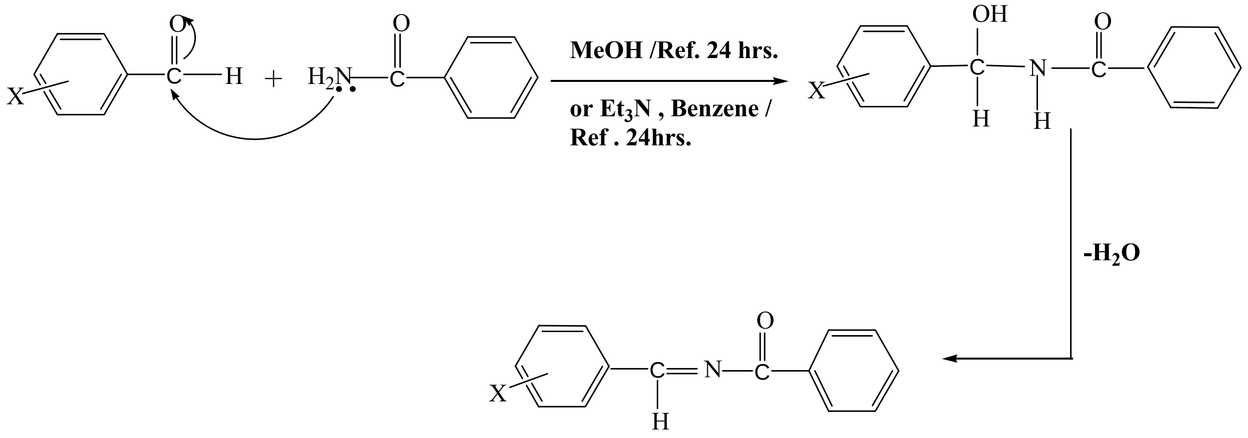


X= H, 4-Cl, 4-OMe, 2-Cl, 2, 6-di-Cl, 3,4-di-OMe,

2,3-di-OMe, 2,4-di-OMe, 2-OH,3-NO_2

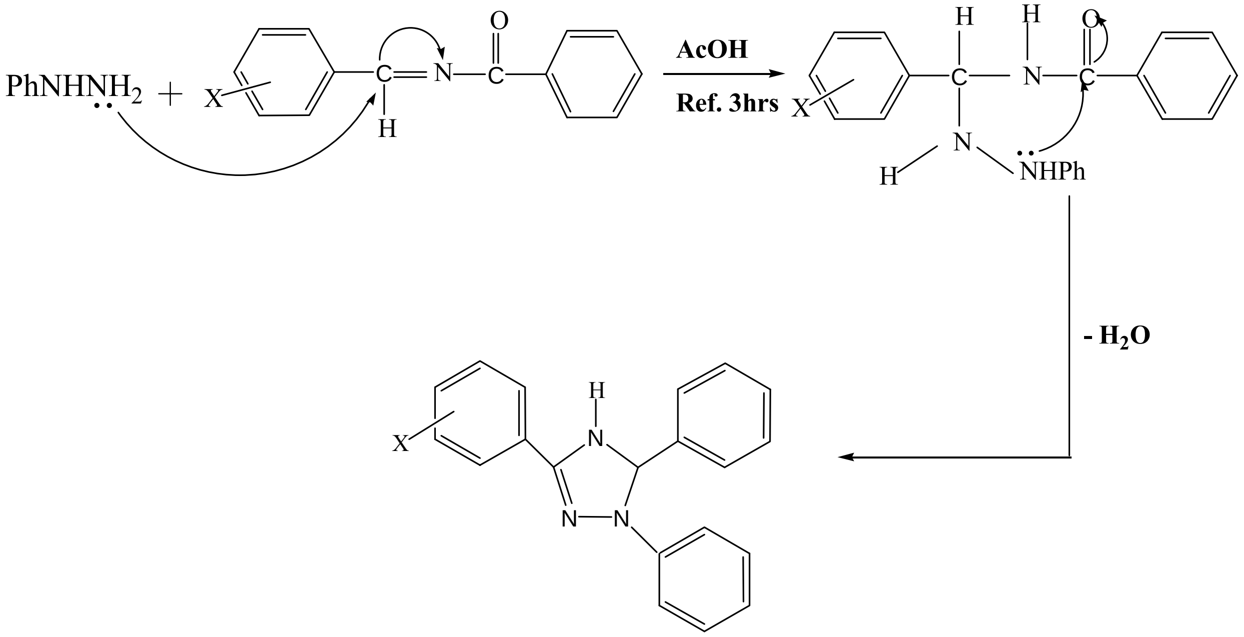
Scheme (1)

According to the scheme, arylidenebenzamide (1-10) synthesized through the condensation of benzamide with aromatic aldehyde (methods A and B) as shown in the following mechanism:



The IR spectra for these compounds show two significant absorption bands in the region (1651-1660cm^{-1}) for (C=O) function and (1575-1578cm^{-1}) for (C=N) function, the depresion of the absorption frequencies of both (C=O) and (C=N) is attributed to the resonance in the conjucated system. The UV spectra give λ max at (282-284nm), and here again the increasing of λ max is due to conjugation (Parikh, 1974).

Arylidenebenzamide react with phenylhydrazine in acidic medium in the same manner that it's carbon analogue (Arylidenacetophenone) does. The reaction proceeds through Michael addition (1,4-addition), which involve nucleophilic attack of the electron pair of N-2 atom of the neutral molecule, $PhNHNH_2$ to the carbon atom of (C=N) group of the conjugated system , followed by cyclization which affords the triazoles (11-20) (Katritzky and Rees, 1984; Said, 1998) which can be illustrated by the following mechanism:



The spectral data for the synthesised compounds (11-20) are in quite good agreement with their proposed structures. The IR spectra shows two significant absorption bands in the region (3421-3456 cm^{-1}) for (N—H) function and (1574-1593 cm^{-1}) for (C=N) function, furthermore in this spectra the absence of (C=O) absorption band of the parent compounds (1-10) clearly indicated the fusing between compounds (1-10) and phenylhydrazine. Finally the UV spectra for these compounds give λ max at (286-300nm).

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