SYNTHESIS OF NOVEL PYRAZOLE DERIVATIVES FROM DIARYL 1,3-DIKETONES (PART-II)

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ABSTRACT : Some 3,5-disubstituted pyrazoles derivatives **(2a-2f)** have been synthesized. Their structure were confirmed by elemental analysis, IR, ^{1}H NMR, ^{13}C NMR and MS spectral studies.

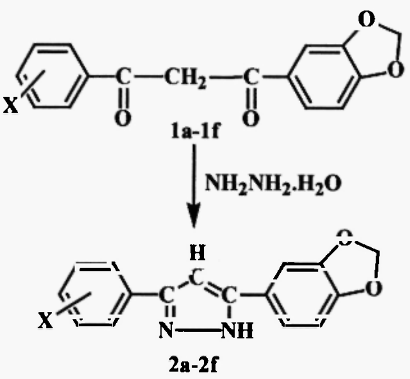
INTRODUCTION

In the last five decades, the pyrazole ring has attracted much attention as it has become fairly accessible and shows diverse biological activity (1-2). The importance of pyrazole lies in the fact that they can be effectively used as anti-inflammatory (3), analgesics, anticonvulsant (4) and antibacterial agents (5). The 1,3-benzodioxole moiety has shown interesting and diversities properties when used to obtain new biologically active drugs (6-7). In continuation of our work (8) on synthesis of pyrazole derivative with 1,3-benzodioxole unit as one substituent here we report synthesis and characterization of 3,5-disubstituted pyrazole derivatives.

RESULT AND DISCUSSION

Derivatives of propane-1-(1,3-benzodioxol-5-yl)-3-phenyl-1,3-dione **(1a-1f)** when condensed with hydrazine hydrate, in absolute ethanol results in formation of schiff base type compound having pyrazole nucleus. Hydrazine hydrate beside being reactant also make the media basic, to promote the enol form of mentioned diketone. The structure of the synthesized compound are well supported by spectroscopic data (Scheme-1, Table-1).

	X
a	3-Cl
b	3-NH_2
c	3-NO_2
d	3,4-Cl
e	3,4-Br
f	3,4-OCH_3



Scheme-1

SPECTRAL STUDIES

In IR spectra, absorption at 1420 cm^{-1} have been assigned to C=N stretching in five membered heterocyclic ring. Characteristic –NH stretching vibration was observed around 3250 cm^{-1} The bands appearing in the region 1265-1235 cm^{-1} and 1060-1035 cm^{-1} are due to C-O-C asymmetric and symmetric vibrations respectively.

In ^{1}H NMR, a singlet is obtained for dioxymethylene protons at δ 6.02-6.07. All the synthesized compound exhibit a single sharp peak in the region δ 7.21-7.34 due to –NH proton. Methine proton at δ 6.69-6.79 as singlet further confirms the formation of pyrazole ring. The aromatic protons were indicated at δ 6.6-8.3 as multiplets. A singlet is also observed at δ 3.79 due to the protons of –OCH_3 group in the respective compound **2f**. The ^{1}H NMR data of the title compounds are given in Table-2.^{13}C NMR data for the compounds (**2a-2f**) is presented in Table-3 and these data are in good agreement with their structure.

Mass spectra of compounds (**2a-2f**) gave the molecular ion peaks (m/z) which corresponded to their molecular weight. A culture of ion peaks to $[M]^+$, $[M+2]^+$ at 298, 300 were observed in case **2a**. The $[M+2]^+$ peaks was nearly one fourth of $[M]^+$ peaks indicating the presence isotopic Cl^{37}.

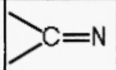
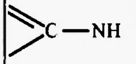
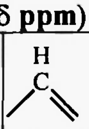
Table – 1: Elemental analysis data of title compounds.

Compd.	M.F.	M.W.	Elemental Analysis Calcd. and (Found)				M.P. (°C)
			C%	H%	N%	X%	
2a	$C_{16}H_{11}N_2O_2Cl$	298.5	64.32 (64.01)	3.69 (3.51)	9.38 (9.11)	11.89 (11.33)	153
2b	$C_{16}H_{13}N_3O_2$	279	68.82 (68.63)	4.66 (4.25)	15.05 (14.86)	-	177
2c	$C_{16}H_{11}N_3O_4$	309	62.14 (61.88)	3.56 (3.38)	13.59 (13.17)	-	134
2d	$C_{16}H_{10}N_2O_2Cl_2$	333	57.66 (57.32)	3.00 (2.94)	8.41 (8.06)	21.32 (21.14)	105
2e	$C_{16}H_{10}N_2O_2Br_2$	421	45.61 (45.43)	2.36 (2.22)	6.65 (6.39)	37.53 (37.26)	118
2f	$C_{18}H_{16}N_2O_4$	324	66.67 (66.35)	7.94 (4.73)	8.64 (8.50)	-	143

Table – 2: ^1H NMR data of title compounds (in δ ,ppm)

Compd.	Ar-X	-NH 1H, (s)	Methine 1H, (s)	OCH_2O 2H, (s)	Aromatic Protons
2a	-	7.21	6.72	6.03	6.90-7.99
2b	4.84 (b), 2H,s	7.30	6.71	6.07	6.92-7.83
2c	-	7.33	6.69	6.08	6.93-8.32
2d	-	7.31	6.76	6.02	6.85-7.86
2e	-	7.28	6.79	6.02	6.91-7.99
2f	3.79, 6H s	7.34	6.75	6.05	6.88-7.75

Table – 3: ^{13}C NMR data of title compounds. (in δ ppm)

Cpd.	Ar-X	O(C)O				Ar at C_3	Ar at C_5
2a	-	101.3	150.7	136.5	97.5	139.7-118.3	147.5-105.3
2b	-	101.8	151.0	136.2	97.4	151.4-114.6	147.6-105.4
2c	-	101.9	150.4	135.8	97.1	152.0-117.5	147.5-105.7
2d	-	101.4	150.4	136.0	97.0	142.3-116.1	147.5-105.4
2e	-	101.7	151.0	135.7	97.8	140.1-115.3	147.4-105.2
2f	OCH_3-55.2	101.5	150.6	136.3	97.4	153.6-112.7	147.6-105.6

EXPERIMENTAL

Melting points are uncorrected. The IR spectra were recorded in KBr disk on a Nicolet Megna-FT-IR 550 spectrometer. ^{1}H NMR and ^{13}C NMR were recorded on model DRX300 at 300.13 and 75.48 MHz, respectively, in $CDCl_3$/DMSO-d_6 using TMS as internal standard. Mass spectra were recorded on Jeol D-300 spectrometer. The purity of the newly synthesized compounds were checked by TLC.

GENERALIZED PREPARATION OF PYRAZOLE DERIVATIVES

A mixture of β-diketone (0.0625 M) and hydrazine hydrate (4.9g, 0.1 M) was refluxed in absolute ethanol (80 ml) for approx. four hours on steam bath. The mixture is cooled and filtered. Crystallization with ethanol yields the crystalline product. Purity of compounds is checked by TLC using ($CHCl_3$: CH_3OH, 9:1) as mobile phase.

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