Synthesis and Mass Spectral Studies of 1-[5-Chloro-1-substituted-2(1*H*)-pyrazin-2-on-3-yl]-5-aryl-3-methylpyrazoles

B. K. Bhattacharya* and F. R. Eirich

Department of Chemistry, Polytechnic Institute of New York,
333 Jay Street, Brooklyn, New York 11201, USA

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Sixteen new 1-[5-chloro-1-substituted-2(1*H*)-pyrazin-2-on-3-yl]-5-aryl-3-methylpyrazoles V have been synthesized by condensation of 5-chloro-1-substituted-3-hydrazino-2(1*H*)-pyrazin-2-ones III and 1-aryl-1,3-butanediones IV in dry 1,4-dioxane. The general mass spectral fragmentation mode of these compounds has been studied.

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Introduction.

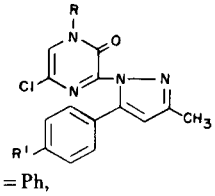
The pyrazines, pyrazinones and pyrazoles are associated with antibacterial, antifungal, antileukemic and antiinflammatory activity [1-5]. It was considered worthwhile to undertake the synthesis and mass spectral studies of some previously unreported 1-[5-chloro-1-substituted-2(1*H*)-pyrazin-2-on-3-yl]-5-aryl-3-methylpyrazoles V.

The 1-[5-chloro-1-substituted-2(1*H*)-pyrazin-2-on-3-yl]-5-aryl-3-methylpyrazoles V were synthesized by condensation between 5-chloro-1-substituted-3-hydrazino-2(1*H*)-pyrazin-2-ones III and 1-aryl-1,3-butanediones IV in dry 1,4-dioxane under normal experimental conditions following the versatile method of pyrazole synthesis [6]. The 5-chloro-1-substituted-3-hydrazino-2(1*H*)-pyrazin-2-ones III needed in this synthesis were conveniently synthesized by the reaction of dry hydrazine on the respective 3,5-dichloro-1-substituted-2(1*H*)-pyrazinones II. The 1-aryl-1,3-butanediones were synthesized following the method of Hauser *et al.* [7] by a Claisen condensation reaction between ethyl acetate and the corresponding acetones. The 3,5-dichloro-1-substituted-2(1*H*)-pyrazinones IIa-d required in this synthesis were synthesized by cyclization of the respective 2-substituted aminoacetonitrile hydrochlorides Ia-d in ODCB (*o*-dichlorobenzene) at temperatures between 80 to 100° following the method of Vakemans *et al.* [8].

The structure of the title compounds was confirmed by their elemental analyses, ir, ^{1}H-nmr and mass spectral data. The ir spectra were taken in potassium bromide discs and the ^{1}H-nmr spectra were taken in DMSO-d_6 with

Table 1

Significant Mass Spectral Data Showing Fragmentation Ions of the Compounds VI, V5, V9 and V13



VI, R = Me, R^1 = H		V5, R = Ph, R^1 = H		V9, R = Bz, R^1 = H		V13, R = Cyhclohex, R^1 = H	
m/z	(%)	m/z	(%)	m/z	(%)	m/z	(%)
300	(90)	362	(100)	376	(85)	368	(100)
285	(29)	347	(28)	361	(30)	353	(28)
272	(30)	334	(18)	348	(20)	340	(30)
259	(64)	321	(61)	257	(10)	257	(15)
258	(10)	320	(15)	230	(30)	230	(25)
257	(13)	294	(30)	165	(11)	165	(18)
243	(15)	257	(13)	129	(16)	129	(16)
232	(45)	243	(13)	103	(18)	103	(28)
230	(17)	230	(28)	90	(25)	90	(22)
182	(16)	182	(20)	77	(10)	77	(13)
165	(8)	165	(5)				
129	(15)	129	(10)				
103	(6)	103	(9)				
90	(28)	90	(18)				
77	(12)	77	(15)				

Me = CH_3, Ph = C_6H_5, Bz = C_6H_5-CH_2-, Cyclohex = Cyclohexyl.

TMS as the internal reference.

In the ir spectrum, the compounds V neither showed absorption bands in the region between 1640-1670 cm^{-1} nor in the region between 3200-3400 cm^{-1} which clearly confirms the absence of C=O and -NH-NH_2 groups in the molecule and its cyclization product. The signal of the 3-methyl group of the pyrazole ring in the compound V1, appeared at δ 2.42 ppm as a singlet and other signals of the N-CH_3 (pyrazinone ring), C-4 proton of pyrazole ring, H-6 proton of pyrazinone ring and C-5 aryl protons (pyrazole ring) appeared at δ 3.45 ppm as a singlet, δ 6.41 ppm as singlet, δ 7.38 ppm as a singlet and δ 7.45 ppm as a multiplet respectively.

The 3-methyl group of the pyrazole ring which appears as a singlet at δ 2.42-2.55 ppm in the compounds V1-16, may be located either at position C-3 or C-5 of the pyrazole ring since there are two possibilities of attack of the hydrazino compounds III to the 1-aryl-1,3-butanediones IV. According to the first possibility, if the hydrazino compound III attacks the carbonyl group of the 1-aryl-1,3-butanedione IV adjacent to the methyl group, it would result in the formation of 1-[5-chloro-1-substituted-2(1*H*)-pyrazin-2-on-3-yl]-5-aryl-3-methylpyrazole V but on the other hand if the attack of the hydrazino compound III takes place on the carbonyl group of the compound 1-aryl-1,3-butanedione IV, adjacent to the phenyl ring, it would result in the formation of 1-[5-chloro-1-substituted-2(1*H*)-pyrazin-2-on-3-yl]-3-aryl-5-methylpyrazole (VI). We have confirmed this in our investigation that reaction of 5-chloro-1-substituted-3-hydrazino-2(1*H*)-pyrazinones IIIa-d and 1-aryl-1,3-butanediones IV in 1,4-dioxane gave 1-[5-chloro-1-substituted-2(1*H*)-3-aryl-5-methylpyrazoles VI which indicates that the carbonyl group of the 1-aryl-1,3-butanediones IV, adjacent to the methyl group is probably more reactive than the carbonyl group adjacent to the phenyl ring.

The formation of 1-[5-chloro-1-substituted-2(1*H*)-pyrazin-2-on-3-yl]-5-aryl-3-methylpyrazoles V instead of 1-[5-chloro-1-substituted-2(1*H*)-pyrazin-2-on-3-yl]-3-aryl-5-methylpyrazoles VI is further supported by their mass spectra. The mass spectrum of compound V1 revealed that most abundant fragment ion m/z 259 (64%) is only due to the loss of CH_3CN from the molecular ion m/z 300 (90%) (base peak). This type of fragmentation is only possible when the CH_3 group is present at the C-3 position of the pyrazole

Table 2

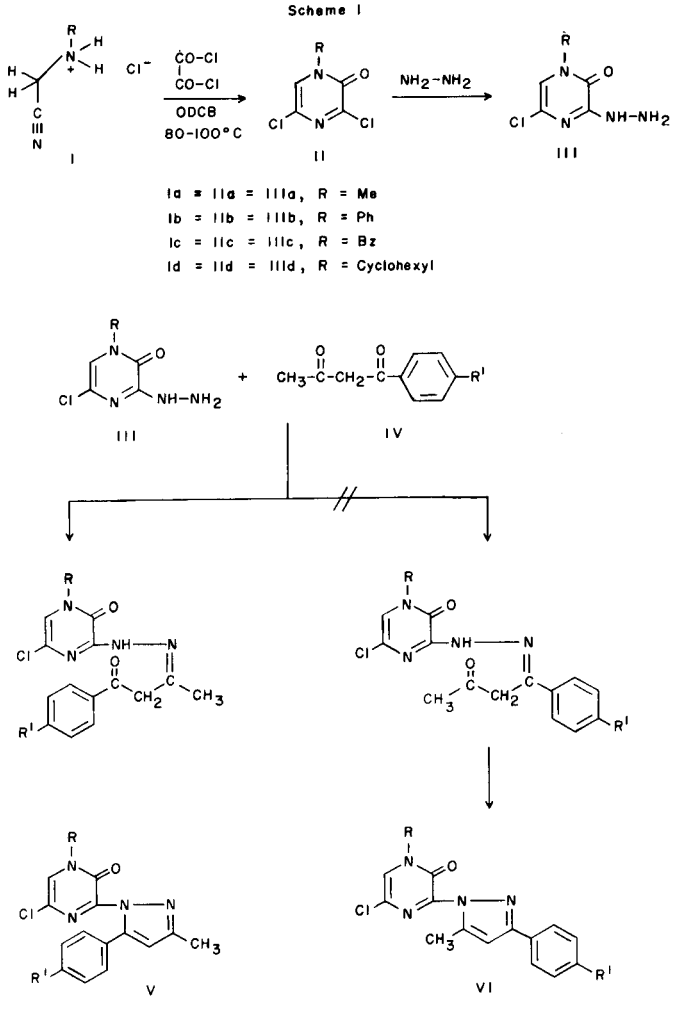
Compound No.	R	R¹	Molecular formula	Mp, (°C)	Yield (%)	Analysis (%) Calcd./(Found) C	H	N
V1	Me	H	$C_{15}H_{12}ClN_4O$	165	70	60.00 (60.18)	4.33 (4.25)	18.66 (18.46)
V2	Me	Cl	$C_{15}H_{12}Cl_2N_4O$	145	73	53.89 (53.75)	3.59 (3.64)	16.76 (16.56)
V3	Me	Br	$C_{15}H_{12}ClBrN_4O$	178	68	47.49 (47.54)	3.17 (3.25)	14.78 (14.75)
V4	Me	O-CH_3	$C_{16}H_{15}ClN_4O_2$	182	75	58.18 (58.28)	4.55 (4.35)	16.85 (16.82)
V5	Ph	H	$C_{20}H_{25}ClN_4O$	210	65	66.29 (66.48)	5.73 (5.65)	15.47 (15.35)
V6	Ph	Cl	$C_{20}H_{14}Cl_2N_4O$	185	61	60.45 (60.48)	3.53 (3.56)	14.12 (14.12)
V7	Ph	Br	$C_{20}H_{14}ClBrN_4O$	205	55	54.29 (54.35)	3.16 (3.01)	12.66 (12.45)
V8	Ph	O-CH_3	$C_{21}H_{17}ClN_4O_2$	195	58	64.29 (64.31)	4.33 (4.32)	14.29 (14.12)
V9	Bz	H	$C_{21}H_{17}ClN_4O$	180-183 dec	65	67.02 (67.22)	4.52 (4.65)	14.91 (14.91)
V10	Bz	Cl	$C_{21}H_{16}Cl_2N_4O$	215	48	61.31 (61.33)	3.89 (3.91)	13.62 (13.65)
V11	Bz	Br	$C_{21}H_{16}ClBrN_4O$	220 dec	68	56.04 (56.12)	3.51 (3.55)	12.31 (12.33)
V12	Bz	O-CH_3	$C_{22}H_{19}ClN_4O_2$	208	74	65.02 (65.12)	4.73 (4.66)	13.80 (13.82)
V13	Cyclohex	H	$C_{20}H_{21}ClN_4O$	184	80	65.22 (65.35)	5.71 (5.75)	15.22 (15.35)
V14	Cyclohex	Cl	$C_{20}H_{20}Cl_2N_4O$	170	67	59.55 (59.65)	4.96 (4.82)	13.90 (13.93)
V15	Cyclohex	Br	$C_{20}H_{20}ClBrN_4O$	200-202 dec	60	53.69 (53.56)	4.47 (4.82)	12.53 (12.65)
V16	Cyclohex	O-CH_3	$C_{21}H_{23}ClN_4O_2$	187	68	63.32 (63.42)	5.78 (5.68)	14.07 (14.18)

Me = Methyl, Ph = Phenyl, Bz = Benzyl, Cyclohex = Cyclohexyl.

ring otherwise one should observe the loss of C_6H_5CN from the molecular ion of the alternate structure VI having a phenyl group at the C-3 position of the pyrazole ring. The same type of loss of CH_3CN also takes place from the molecular ion m/z 362 (100%) of the compound V5 which further confirms the position of the methyl group at C-3 and not at C-5 in the pyrazole ring. Further, it has been reported earlier by Barry *et al.* [9] that reaction of benzoyl acetate with *p*-chlorophenylhydrazine yields the formation of 1-(*p*-chlorophenyl)-5-phenyl-3-methylpyrazole rather than 1-(*p*-chlorophenyl)-3-phenyl-5-methylpyrazole probably due to the carbonyl group in ethyl acetate, adjacent to the alkyl group, is relatively more reactive than the carbonyl group adjacent to the phenyl ring which is in complete agreement with our observations and supports the formation of 1-[5-chloro-1-substituted-2(1*H*)-pyrazin-2-on-3-yl]-5-aryl-3-methylpyrazoles V rather than 1-[5-chloro-1-substituted-2(1*H*)-pyrazin-2-on-3-yl]-3-aryl-5-methylpyrazoles VI.

The synthesis of the title compounds are depicted in Scheme 1.

Scheme I



Study of the Mass Spectral Fragmentation Mode.

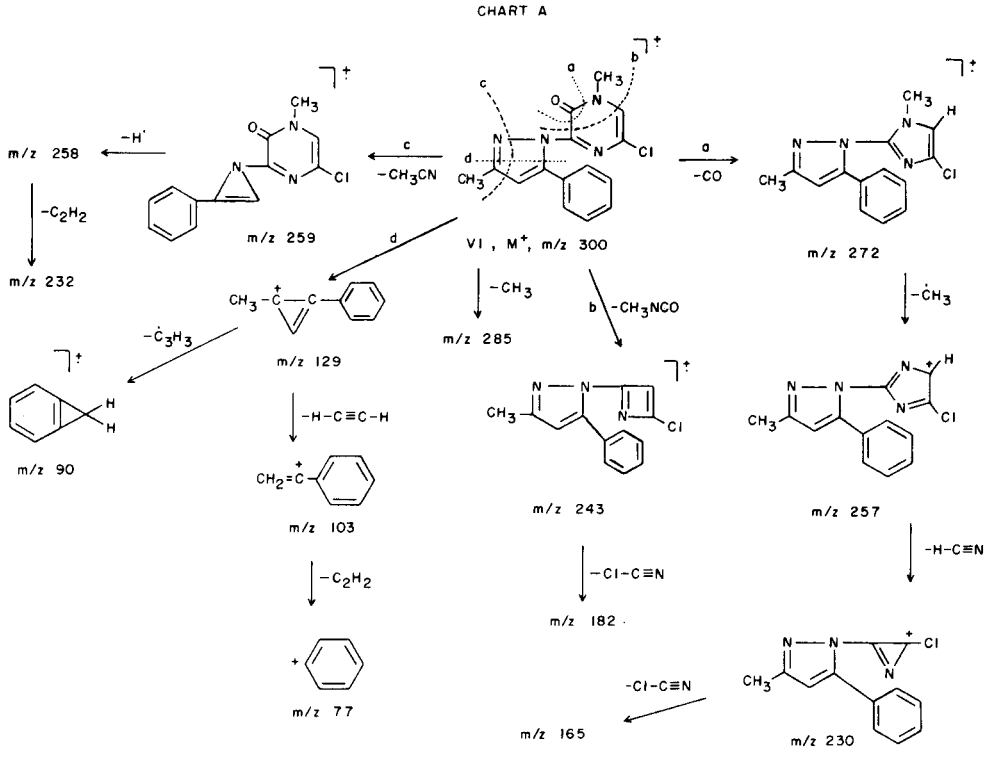
The mass spectral fragmentation of these compounds generally undergoes fission of the molecular ion *via* four principal modes: (i) Fission of the pyrazinone ring *via a* with the concominant loss of the carbonyl group from the molecular ion; (ii) Fission of pyrazinone ring *via b* with the loss of CH_3-N=C=O from the molecular ion; (iii) Fission of pyrazole ring *via c* with the concominant loss of CH_3CN from the molecular ion; and (iv) Fission of pyrazole ring *via d* with the loss of pyrazinonyl diazonium radical. The mass spectrum of 1-[5-chloro-1-methyl-2(1*H*)-pyrazin-2-on-3-yl]-5-phenyl-3-methylpyrazole (V1) showed the molecular ion at m/z 300, which appeared as the base peak. The fission of pyrazinone ring in this compound *via a* yielded an ion at m/z 272 (30%) due to the loss of CO from the molecular ion and this ion again loses the CH_3 radical to yield an ion at m/z 257 (13%) which further loses H-C≡N to yield an ion at m/z 230, this ion, due to loss of Cl-C≡N, yields an ion at m/z 165 which coincides with the known mass spectral fragmentation of 3,5-dichloro-1-methyl-2(1*H*)-pyrazinone [8]. On the other hand we have found an ion at m/z 243 due to the loss of CH_3-N=C=O from the molecular ion after the fission of pyrazinone ring *via b*, and this ion again loses Cl-C≡N to yield an ion at m/z 182.

The fission of the pyrazole ring in this compound V1 *via c* involved in the loss of CH_3CN from the molecular ion which results in the formation of an intense ion at m/z 259, loses a hydrogen radical and an acetylene to yield ions at m/z 258 and m/z 232 respectively. In a typical fragmentation, the fission of pyrazole ring *via d* suffers a cleavage with the expulsion of 2-pyrazinonyldiazonium radical from the molecular ion. Thus, the ion at m/z 129, loses acetylene and yields an ion at m/z 103 which further loses acetylene resulting in a phenyl cation at m/z 77. However, the cation at m/z 129 also undrgoes a loss of the propylene radical to yield a peak of the benzocyclopropenyl ion at m/z 90.

The same type of mass spectral fragmentaion mode is found in case of 1-[5-chloro-1-phenyl-2(1*H*)-pyrazin-2-on-3-yl]-5-phenyl-3-methylpyrazole (V5) which gave prominant ions at m/z 362, 321, 294, 347, 334, 257, 230, 165, 243, 182, 129, 103, 90 and 77 corresponds to the ions of the compound V1 at m/z 300, 259, 258, 232, 285, 272, 257, 230, 165, 243, 182, 129, 103, 90 and 77 respectively. This observation strongly supports the similarity in the degradative sequence of both of the compounds V5 and V1. The mass spectral fragmentation mode of compound V1 is rationalized by the sequences outlined in Chart A.

However, in the mass spectrum of compounds V9 and V13, it has been observed that the fragmentation pattern is slightly different in comparison with the compounds V1 and V5. In these cases, compounds V9 and V13, the fission pattern of the pyrazole ring *via c* and *d* was exactly the same as it was in the case of compounds V1 and V5 but the

CHART A



fission pattern of the pyrazinone ring did not follow exactly *via a* and *b*. For example in the compound V9, the fission of pyrazinone ring was *via a* and loses C=O from the molecular ion to yield an ion at m/z 348 which suffers a cleavage of the pyrazole ring but yields an ion at m/z 257 due to loss of the benzyl radical which further loses H-C≡N to give an ion at m/z 230 and this ion further loses Cl-C≡N to give an ion at 165. On the other hand there is not any peak at m/z 243 which clearly indicates that there is no loss of Bz-N=C=O from the molecular ion and the molecule suffers cleavage of pyrazinone ring *via b*.

The significant mass fragmentation ions of the compounds V1, V5, V9 and V13 are given in Table 1.

EXPERIMENTAL

The melting points were recorded on a Fisher-Johns apparatus and are uncorrected. The ir spectra were recorded on a Perkin-Elmer spectrophotometer model 257 and ^{1}H-nmr were recorded on a Perkin-Elmer Hitachi R-600, 60 MHz, and Varian XL-100 spectrophotometers using TMS as the internal reference. The mass spectra were taken on an AEI-MS-12 (ionization energy 70 eV) apparatus. All compounds were dried *in vacuo* at 80° for 10 to 15 hours before elemental analyses. The elemental analyses were performed on a Perkin-Elmer 240 elemental analyzer.

2-Methylaminoacetonitrile Hydrochloride (Ia).

This compound was commercially available and used as such without any further purification.

2-Phenylamino-, 2-Benzylamino- and 2-Cyclohexylaminoacetonitrile Hydrochlorides Ib-d.

These were prepared following the literature procedure [8,10].

3,5-Dichloro-1-substituted-2(1*H*)-pyrazinones IIa-d.

These were synthesized by cyclization of the corresponding hydrochlorides of 2-substituted aminoacetonitriles Ia-d with oxalyl chloride in ODCB at 80-100° following the method fo Vekemans *et al.* [8], and purified on silica gel using an acetonitrile-dichloromethane mixture for elution. These were recrystallized from diethyl ether-dichloromethane (IIa), hexane-dichloromethane (IIb), diethyl ether (IIc) and hexane (IId).

5-Chloro-3-hydrazino-1-substituted-2(1*H*)-pyrazin-2-ones IIIa-d.

In a general procedure 320 mg (10 mmoles) of freshly distilled dry hydrazine were added to a solution of 3,5-dichloro-1-substituted-2(1*H*)-pyrazinone II (460 mg, 2.6 mmoles) dissolved in 25 ml of dry 1,4-dioxane. The reaction mixture was stirred for 3 hours at 20° under nitrogen atmosphere. To this reaction mixture, 500 mg of sodium carbonate was added and the reaction mixture was again stirred for another 1 hour at 20°. The reaction mixture was kept overnight in the refrigerator and filtered. The precipitate thus obtained was removed by filtration and washed with methanol (20 ml) and again filtered. The filtrates were combined together and concentrated *in vacuo*. The residue thus obtained was recrystallized from ethanol.

The analytical data of compounds IIIa-d are summarized below.

Compound IIIa.

This compound was obtained in a yield of 65%, mp 171°; ir (potassium bromide): ν cm^{-1} 1680 (C=O), 1672 (lactam C=N), 3200 (sb, NH), 860 (=C-H); ^{1}H-nmr (DMSO-d_6): δ 3.62 (s, 3H, N-CH_3), 7.432 (s, 1H, H-6), 3.42 (s, br, 2H, NH_2), 8.55 (s, br, 1H, NH); ms: m/z 174.

Anal. Calcd. for $C_5H_7ClN_4O$: C, 34.48; H, 4.02; N, 32.18. Found: C, 34.45; H, 3.99; N, 32.34.

Compound IIIb.

This compound was obtained in a yield of 71%, mp 168°; ir (potassium bromide): ν cm^{-1} 1685 (C=O), 1672 (lactam C=N), 3200 (sb, NH), 865

Table 3

Compound No.	IR (cm^{-1}) C=O	(Potassium Bromide) C=N	MS m/z	Relative Abundance (%)	^{1}H-NMR (DMSO-d_6), δ ppm
V1	1680	1665	300	90	3.45 (s, 3H, N-CH_3), 2.42 (s, 3H, C-3, -CH_3), 6.41 (s, 1H, C-4, pyrazole-H), 7.38 (s, 1H, H-6 pyrazinone-H), 7.45 (m, 5H, C-5 aryl-H)
V2	1682	1660	334	70	3.41 (s, 3H, N-CH_3), 2.45 (s, 3H, C-3, CH_3), 6.44 (s, 1H, C-4, pyrazole-H), 7.28 (s, 1H, H-6 pyrazinone-H), 7.52 (m, 4H, C-5, aryl-H)
V3	1685	1660	381	80	3.42 (s, 3H, N-CH_3), 2.45 (s, 3H, C-3, CH_3, pyrazole), 6.43 (s, 1H, C-4, pyrazole-H), 7.29 (s, 1H, H-6, pyrazinone-H), 7.52 (m, 4H, C-5, aryl-H)
V4	1680	1660	330	100	3.44 (s, 3H, N-CH_3), 2.44 (s, 3H, C-3, CH_3), 6.44 (s, 1H, C-4, pyrazole-H), 7.24 (s, 1H, H-6, pyrazinone-H), 7.48 (m, 4H, C-5, aryl-H), 2.33 (s, 3H, *p*-OCH_3)
V5	1685	1670	362	100	7.52 (m, 5H, N-C_6H_5), 7.31 (s, 1H, H-6, pyrazinone-H), 2.45 (s, 3H, C-3, CH_3), 6.42 (s, 1H, C-4, pyrazole), 7.41 (m, 5H, C-5, aryl-H)
V6	1680	1665	397	65	7.48 (m, 5H, N-C_6H_5), 7.23 (s, 1H, H-6, pyrazinone-H), 2.42 (s, 3H, C-3, CH_3), 6.41 (s, 1H, C-4, pyrazole-H), 7.51 (m, 4H, C-5, aryl-H)
V7	1680	1660	443	45	7.49 (m, 5H, N-C_6H_5), 7.31 (s, 1H, H-6, pyrazinone), 2.45 (s, 3H, C-3, CH_3), 6.48 (s, 1H, C-4, pyrazole-H), 7.51 (m, 4H, C-5, aryl-H)
V8	1682	1666	392	65	7.52 (m, 5H, N-C_6H_5), 7.18 (s, 1H, H-6, pyrazinone-H), 2.43 (s, 3H, C-3, CH_3), 6.44 (s, 1H, C-4, pyrazole-H), 2.32 (s, 3H, *p*-OCH_3), 7.46 (m, 4H, C-5, aryl-H)
V9	1685	1665	376	85	7.50 (m, 5H, N-C_6H_5-CH_2), 5.12 (s, 2H, -CH_2-Ph), 7.31 (s, 1H, H-6, pyrazinone-H), 2.46 (s, 3H, C-3, CH_3), 6.45 (s, 1H, C-4, pyrazole-H), 7.45 (m, 5H, C-5, aryl-H)
V10	1680	1675	411	80	7.48 (m, 5H, C_6H_5-CH_2-N), 5.11 (s, 2H, -CH_2-Ph), 7.24 (s, 1H, H-6, pyrazinone-H), 2.44 (s, 3H, C-3, -CH_3), 6.44 (s, 1H, C-4, pyrazole-H), 7.52 (m, 4H, C-5, aryl-H)
V11	1680	1670	455	100	7.49 (5H, C_6H_5-CH_2-N), 5.24 (s, 2H, CH_2-Ph), 2.45 (s, 3H, C-3, CH_3), 6.44 (s, 1H, C-4, pyrazole-H), 7.18 (s, 1H, H-6, pyrazinone-H), 7.51 (m, 4H, C-5, aryl-H)
V12	1680	1660	406	90	7.53 (m, 5H, C_6H_5-CH_2-N), 5.12 (s, 2H, -CH_2-Ph), 7.32 (s, 1H, H-6, pyrazinone-H), 2.44 (s, 3H, C-3, CH_3), 6.45 (s, 1H, C-4, pyrazole-H), 7.46 (m, 4H, C-5, aryl-H), 2.33 (s, 3H, *p*-OCH_3)
V13	1685	1660	368	100	2.55 (s, 3H, CH_3), 2.35 (m, 10H, *N*-cyclohexyl), 4.65 (br, m, 1H, *N*-cyclohexyl-1H), 7.25 (s, 1H, H-6, pyrazinone-H), 6.45 (s, 1H, C-4, pyrazole-H), 7.46 (m, 5H, C-5, aryl-H)
V14	1680	1662	403	85	2.45 (s, 3H, -CH_3), 2.36 (m, 10H, *N*-cyclohexyl-H), 4.65 (br, m, 1H, *N*-cyclohexyl-1H), 7.35 (s, 1H, H-6, pyrazinone-H), 7.55 (m, 4H, C-5, aryl-H), 6.42 (s, 1H, C-4, pyrazole-H)
V15	1680	1665	447	55	2.44 (s, 3H, C-3, CH_3), 2.35 (m, 10H, 4.74 (br, m, 1H, *N*-cyclohexyl-1H), 7.34 (s, 1H, H-6, pyrazinone-H), 7.48 (m, 4H, C-5, aryl-H), 6.42 (s, 1H, C-4, pyrazole-H)
V16	1682	1660	398	100	2.52 (s, 3H, -CH_3), 2.33 (s, 3H, *p*-OCH_3), 2.43 (m, 10H, *N*-cyclohexyl-H), 7.18 (s, 1H, H-6, pyrazinone-H), 7.48 (m, 4H, C-5, aryl-H), 6.46 (s, 1H, C-4 pyrazole-H)

s = singlet, m = multiplet, br = broad.

(=C-H); ^{1}H-nmr (DMSO-d_6): δ 7.32 (s, 3H, H-6), 7.55 (m, 5H, aryl-H), 3.41 (s, br, 2H, NH_2), 8.50 (s, br, 1H, NH); ms: m/z 236.

Anal. Calcd. for $C_{10}H_9ClN_4O$: C, 50.85; H, 3.81; N, 23.73. Found: C, 50.75; H, 3.85; N, 23.65.

Compound IIIc.

This compound was obtained in a yield of 65%, mp 135°; ir (potassium bromide): ν cm^{-1} 1690 (C=O), 1665 (lactam C=N), 3200 (sb, NH), 885 (=C-H); ^{1}H-nmr (DMSO-d_6): δ 5.12 (s, 2H, CH_2-Ph), 7.38 (s, 1H, H-6), 7.52 (s, br, 5H aromatic), 3.45 (s, br, 2H, NH_2), 8.56 (s, br, 1H, NH); ms: m/z 250.

Anal. Calcd. for $C_{11}H_{11}ClN_4O$: C, 52.6; H, 4.4; N, 22.4. Found: C, 52.16; H, 4.15; N, 22.14.

Compound IIId.

This compound was obtained in a yield of 72% mp 145°; ir (potassium bromide): ν cm^{-1} 1685 (C=O), 1665 (lactam C=N), 3200 (s, br, NH), 885 (=C-H); ^{1}H-nmr (DMSO-d_6): δ 2.35 (m, 10H, cyclohexyl-H), 4.75 (br, m, 1H, H-1), 7.28 (s, 1H, H-6), 3.44 (s, br, 2H, NH_2), 8.52 (s, br, 1H, NH); ms: m/z 242.

Anal. Calcd. for $C_{10}H_{15}ClN_4O$: C, 49.59; H, 6.20; N, 23.14. Found: C, 49.62; H, 6.28; N, 23.24.

1-[5-Chloro-1-substituted-2(1*H*)-pyrazin-2-on-3-yl]-5-aryl-3-methylpyrazoles V.

In a general method, a mixture of 5-chloro-3-hydrazino-1-substituted-2(1*H*)-pyrazin-2-one III (1.74 g, 10 mmoles) and 1-aryl-1,3-butanedione

IV, 2.43 g (15 mmoles) were refluxed in dry 1,4-dioxane in the presence of 0.15 ml of acetic acid for 8 hours. The reaction mixture was cooled to room temperature and kept in the refrigerator overnight. The separated crystals thus obtained were filtered, washed with water, dried and purified by recrystallization from ethanol-hexane (80:20, v/v). The physical constants, analytical data, ir, ^{1}H-nmr and mass spectral data of these compounds are recorded in Table 2 and Table 3.

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