A ^1H and ^{13}C NMR Study of the Structure and Tautomerism of 4-Pyrazolylpyrazolinones

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It has been established that the primary reactions products between dehydroacetic acid and *p*-chlorophenylhydrazine or 4-phenylthiazol-2-ylhydrazine are 4-acetylacetyl-5-hydroxypyrazoles. These compounds react with the above hydrazines to yield 4-(pyrazol-5'-yl)-2-pyrazolin-5-ones which exist in solution as 5-hydroxypyrazoles.

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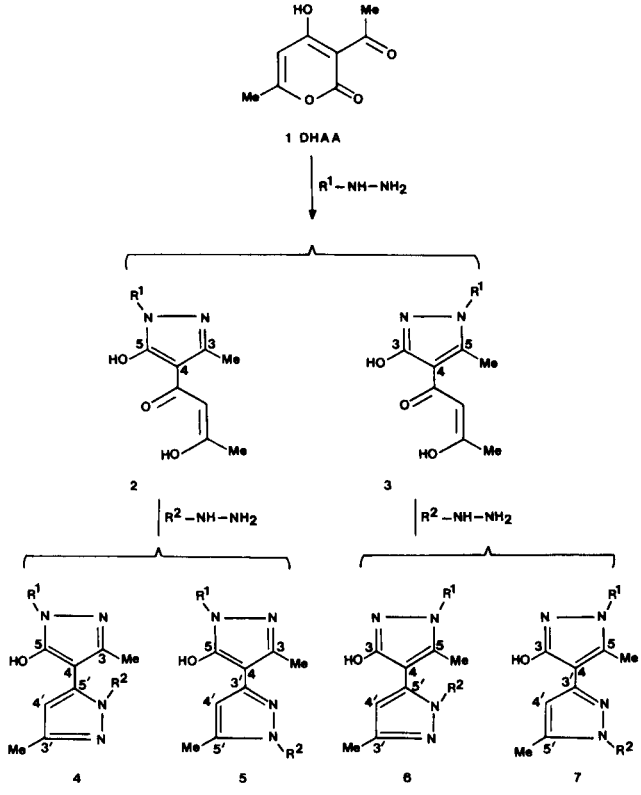
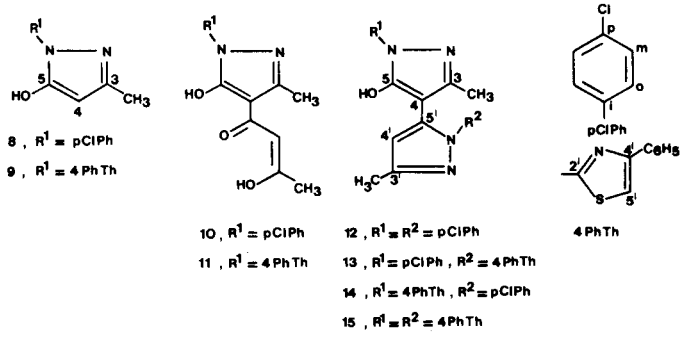
Formally, the reaction of a monosubstituted hydrazine with dehydroacetic acid (DHAA, **1**) can yield, in two steps, four isomeric 4-pyrazolylpyrazolinones (Scheme 1). In general only one compound is formed [1], the aim of this paper being to establish its structure and tautomerism in the case of an aromatic hydrazine (R^1 = *p*-chlorophenyl) and an heterocyclic hydrazine (R^1 = 4-phenylthiazol-2-yl). As the intermediate β-diketone, **2** or **3**, can be isolated, the determination of its structure will simplify the problem of assigning one of the four isomers, **4-7**, to the pyrazolylpyrazolinone.

Scheme 1



Concerning the tautomerism, it is well known [2] that nmr (both ^1H and ^{13}C) is a very simple and convenient method to identify the non-aromatic CH tautomer of pyrazolin-5-ones but that the equilibrium between the NH and OH tautomers of both families of pyrazolinones, the 3- and the 5-products, is difficult to determine. Thus, along this paper, the OH tautomer (hydroxypyrazole) will stand for a mixture of unknown proportions, of NH and OH aromatic tautomers. Four pyrazolylpyrazolinones, two β-diketones and two model compounds, **8** and **9**, bearing the same substituents on the nitrogen were studied in two solvents, deuteriochloroform and hexadeuteriodimethyl sulfoxide.

Scheme 2



Assignment of the Signals in Tables 1 and 2.

Although complicated due to the similar nature of aromatic and heteroaromatic carbons, the assignment methods have become trivial and will be summarized in the following points:

(i) Literature results on pyrazolinones [3], pyrazoles [4], thiazoles [5] and pyrazolyl-β-diketones [6] have been used.

(ii) Internal consistency is important; particularly useful have been dissymetrical compounds **13** and **14** for the assignment of the *N*-substituent signals when $R^1 = R^2$ (**12** and **15**).

(iii) Broad signals characteristic of slow tautomeric equilibria have been useful to distinguish between close

Table 1

^{1}H NMR Chemical Shifts (in ppm) and Coupling Constants (in Hz) of Pyrazolinones

Model Compounds

No.	Solvent	3	4	R^1			Tautomer
8	$CDCl_3$	2.19	3.41	7.83 (H_o)	7.33 (H_m)	J = 9.1	>98% CH
8	DMSO-d_6	2.21	3.32 (bs)	7.83 (H_o)	7.5 (H_m)	J = 9.0	16% CH
		2.10	5.34	7.73 (H_o)	7.44 (H_m)	J = 9.0	84% OH
9	$CDCl_3$	2.26	3.49	7.23 (H_5')	7.90 (H_o)	7.3-7.45 (H_m)	34% CH
		2.23	5.41	7.13 (H_5')	7.75 (H_o)	7.3-7.45 ($H_{m,p}$)	66% OH
9	DMSO-d_6	2.23	5.26	7.73 (H_5')	8.0 (H_o)	7.3-7.5 ($H_{m,p}$)	>95% OH

β–Diketones

No.	Solvent	3	7	8	R^1			Tautomer
10	$CDCl_3$	2.44	5.69	2.11	7.77 (H_o)	7.40 (H_m)	J = 9.0	80% Enol/OH
		2.43	3.87	2.34	7.77 (H_o)	7.40 (H_m)	J = 9.0	20% Keto/OH
10	DMSO-d_6	2.42	6.59	2.04	7.72 (H_o)	7.54 (H_m)	J = 8.8	45% Enol/OH
		2.45	3.84 (bs)	2.13	7.72 (H_o)	7.54 (H_m)	J = 8.8	55% Keto/OH
11	$CDCl_3$	2.55	6.2 (vbs)	2.11	7.22 (H_5')	7.78 (H_o)	7.3-7.4 ($H_{m,p}$)	60% Enol/OH
		2.51	4.03	2.32	7.21 (H_5')	7.74 (H_o)	7.3-7.4 ($H_{m,p}$)	40% Keto/OH
11	DMSO-d_6	2.54	6.67	2.05	7.80 (H_5')	8.03 (H_o)	7.3-7.5 ($H_{m,p}$)	48% Enol/OH
		2.59	4.00	2.20	7.79 (H_5')	8.03 (H_o)	7.3-7.5 ($H_{m,p}$)	52% Keto/OH

4–Pyrazolylpyrazolinones

No.	Solvent	3	3'	4'	R^1			R^2			Tautomer
12 [a]	DMSO-d_6	1.85	2.28	6.31	7.70 (H_o)	7.48 (H_m)	J = 9.0	7.42	7.39	J = 8.8	Tautomer
13	$CDCl_3$	2.33	2.41	6.28	7.87 (H_o)	7.40 (H_m)	J = 9.0	7.29 (H_5')	7.65 (H_o)	7.35 ($H_{m,p}$)	>98% OH
13	DMSO-d_6	2.05	2.31	6.45	7.83 (H_o)	7.55 (H_m)	J = 8.9	7.80 (H_5')	7.88 (H_o)	7.2($H_{m,p}$)	>98% OH
14	$CDCl_3$	1.94	2.39	6.28	7.18 (H_5')	7.77 (H_o)	7.45 ($H_{m,p}$)	7.36	7.73	J = 8.4	>98% OH
14	DMSO-d_6	2.07	2.28	6.34	7.76 (H_5')	8.00 (H_o)	7.45 ($H_{m,p}$)		7.45		>98% OH
15	$CDCl_3$	2.25	2.40	6.30	7.21 (H_5')	7.80 (H_o)	7.4 ($H_{m,p}$)	7.21 (H_5')	7.65 (H_o)	7.4 ($H_{m,p}$)	>98% OH
15	DMSO-d_6 [b]	2.21	2.32	6.46	7.72 (H_5')	8.05 (H_o)	7.4 ($H_{m,p}$)	7.72 (H_5')	7.65 (H_o)	7.1 ($H_{m,p}$)	>98% OH

[bs]Broad signal. [vbs] Very broad signal. [a] This compound is insoluble in deuteriochloroform. [b] Due to its low solubility, this spectrum was recorded at 60°.

signals.

(iv) In a few cases, specific techniques have been used. Thus, a NOE experiment relates the methyl signal at 2.28 ppm with the CH signal at 6.34 ppm (compound **14** in DMSO-d_6), proving that both belong to the pyrazolyl substituent. A heteronuclear ^{1}H-^{13}C COSY experiment with the same compound and solvent justifies the assignment of the methyl signals at the 3 and 3' positions.

Tautomeric Structure of the Model Compounds **8** and **9**.

The behaviour of compound **8** is very similar to that of 1-phenyl-3-methylpyrazolin-5-one [2,3]: >98% CH in deuteriochloroform and 16% CH in DMSO-d_6 (to compare with 100% and 22% CH for the parent compound [3]). The replacement of the *p*-chlorophenyl group by a 4-phenylthiazol-2-yl group increases the percentage of OH tautomer in both solvents, the effect being more important in chloroform than in dimethyl sulfoxide. An intramolecular hydrogen bond (IMHB) shifts the equilibrium towards the OH tautomer in the case of compound **9**, phenomenon already observed in other pyrazolinones. The stabilization of the OH tautomer in deuteriochloroform allows to estimate at about 3 Kcal mol^{-1} the strength of the IMHB. The effect of R^1 is attenuated in dimethyl sulfoxide since there is always an intermolecular hydrogen bond between the OH and the solvent.

Table 2

^{13}C NMR Chemichal Shifts (in ppm) of Pyrazolinones

Model Compounds

No.	Solvent	C_3	C_4	C_5	3-CH_3	R_1							Tautomer
8	$CDCl_3$	156.5	43.0	170.0	16.9	135.9 (C_i)	119.8 (C_o)	128.2 (C_m)	131.2 (C_p)				CH
9	$CDCl_3$	152.9	42.0	170.0	17.0	n.o. (C_2')	n.o. (C_4')	108.0 (C_5')	n.o. (C_i)	126.4 (C_o)	128.5 (C_m)	128.4 (C_p)	CH
		150.3	91.1	154.7	13.7	158.9 (C_2')	133.8 (C_4')	107.3 (C_5')	132.9 (C_i)	126.0 (C_o)	128.8 (C_m)	128.0 (C_o)	OH

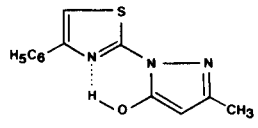
β-Diketones

No.	Solvent	C_3	C_4	C_5	3-CH_3	C_6	C_7	C_8	8-CH_3	R'				Tautomer
10	$CDCl_3$	147.3	100.6	158.8	15.5	188.5	96.8	181.5	22.4	135.9 (C_i)	121.9 (C_o)	129.2 (C_m)	132.1 (C_p)	Enol/OH
		n.o.	n.o.	n.o.	15.2	n.o.	54.6	n.o.	31.0	n.o. (C_i)	n.o. (C_o)	n.o. (C_m)	n.o. (C_p)	Keto/OH
10	DMSO-d_6	150.6	100.2	159.4	114.0	183.3	96.9	n.o.	233.7	134.9 (C_i)	121.5 (C_o)	128.9 (C_m)	129.6 (C_p)	Enol/OH
		150.6	103.9	160.6	13.8	187.4	54.2	186.5	30.1	135.1 (C_i)	121.7 (C_o)	128.9 (C_m)	129.6 (C_p)	Keto/OH
11 [a]	$CDCl_3$	n.o.	n.o.	n.o.	15 (vbs)	n.o.	98.1	n.o.	24.1 (bs)	n.o. (C_2')	n.o. (C_4')	108.0 (C_5')		Enol/OH
										n.o. (C_i)	126.0 (C_o)	128.9 (C_m)	128.9 (C_p)	
		n.o.	n.o.	n.o.	15 (vbs)	n.o.	56.3	n.o.	30.8	n.o. (C_2')	n.o. (C_4')	108.0 (C_5')		Keto/OH
11	DMSO-d_6	152.8	99.1	159.0	13.6	186.3	97.0	183.5	23.6	152.0 (C_2')	148.9 (C_4')	109.2 (C_5')		Enol/OH
										133.6 (C_i)	128.1 (C_o)	128.6 (C_m)	125.9 (C_p)	
		153.3	102.9	160.1	13.3	203.5	55.5	187.9	30.5	152.0 (C_2')	n.o. (C_4')	n.o. (C_5')		Keto/OH

4-Pyrazolylpyrazolinones

No.	Solvent	C_3	C_4	C_5	3-CH_3	C_3'	C_4'	C_5'	3'-CH_3	R^1		R^2		Tautomer
12	DMSO-d_6	148.7	94.4 (bs)	151.9	12.5	147.5	109.7	139.1	13.4	136.8 (bs) (C_i)	121.6 (bs) (C_o)	134.1 (C_i)	134.1 (C_p)	OH
										128.9 (C_m)	129.3 (C_p)	128.8 (C_m)	130.8 (C_p)	
13	DMSO-d_6	148.2	n.o.	150.9	12.7	150.9	110.3	134.6	13.3	137.2 (bs) (C_i)	121.6 (bs) (C_o)	160.1 (C_2')	150.9 (C_4')	OH
										128.8 (C_m)	129.1 (C_p)	111.9 (C_5')	133.8 (C_i)	
												125.5 (C_o)	128.4 (C_m) 127.9 (C_p)	
14	DMSO-d_6	149.7	94.8	152.5	11.3	148.7	109.6	139.2	13.3	158.5 (bs) (C_2')	149.0 (C_4')			
										109.0 (C_5')	133.1 (C_i)	133.7 (C_i)	124.6 (C_m)	OH
										125.9 (C_o)	128.6 (C_m) 128.1 (C_p)	128.8 (C_m)	130.8 (C_p)	
15	$CDCl_3$	151.7	93.7	153.0	13.8	151.9	109.6	134.0	13.7	n.o. (C_2')	152.3 (C_4')	160.9 (C_2')	152.3 (C_4')	OH
										107.5 (C_5')	133.1 (C_i)	111.5 (C_5')	133.5 (C_i)	
										125.9 (C_o)	128.8 (C_m) 128.2 (C_p)	125.2 (C_o)	128.6 (C_m) 127.9 (C_p)	

[bs] Broad singlet. [vbs] Very broad singlet. [n.o.] Not observed. [a] Only slightly soluble in deuteriochloroform.

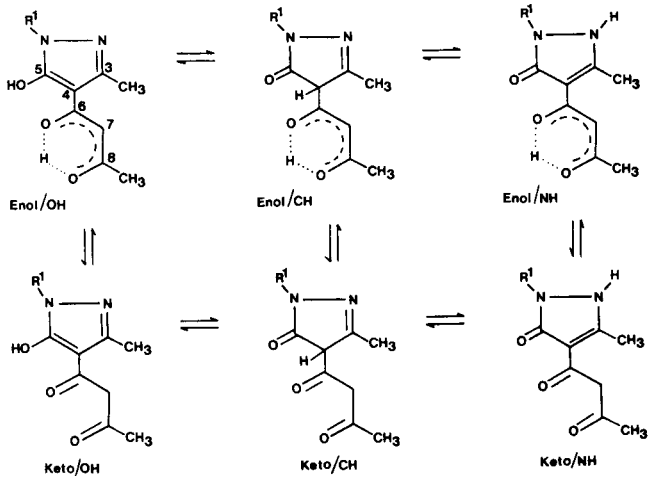


9 (OH-tautomer)

Tautomeric Structure of β-Diketones **10** and **11**.

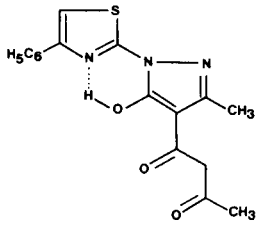
The structure of the parent 3-methyl-4-acetylacetyl-1-phenyl-2-pyrazolin-5-one ($R^1 = C_6H_5$) has been studied in solution (deuteriochloroform and DMSO-d_6) by nmr by Gelin *el al.* [6] and in the solid state by X-ray crystallography by Steel *et al.* [7]. Not considering the enol/enol tautomerism, six forms are possible (Scheme 3). When $R^1 = C_6H_5$ the only observed tautomers in solution are the "enol/OH" and the "keto/OH" [6], whereas in the crystalline only the "enol/OH" tautomer is present [7]. Our nmr

Scheme 3

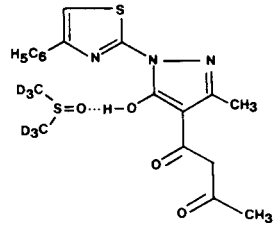


results (Tables 1 and 2) are very similar to those reported by Gelin *et al.* [6]; and since there is no doubt that the compound $R^1 = C_6H_5$ is a pyrazolin-5-one [7], compounds **10** and **11** belongs to the same class of pyrazolinones, *i.e.* they are of type **2** (Scheme 1).

Concerning the keto/enol tautomerism of the β-diketone part, the residue R^1 has little effect on its position (for $R^1 = C_6H_5$, 83% and 50% of "enol/OH" in deuteriochloroform and DMSO-d_6, respectively [6]). In deuteriochloroform, the 4-phenylthiazol-2-yl residue favors the diketo tautomer (Table 1) due to an IMHB, *e.g.* it exerts an effect similar to that of dimethyl sulfoxide. In this last solvent, the 4-phenylthiazol-2-yl group does not affect the keto/enol tautomerism since there is already an intermolecular hydrogen bond between the OH and the "basic" solvent.



11 ($CDCl_3$ solution)



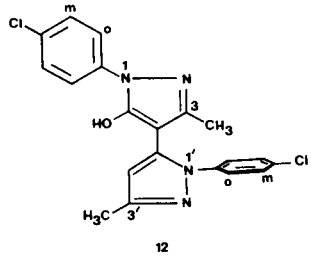
11 (DMSO-d_6 solution)

Compound **11** is only slightly soluble in deuteriochloroform and consequently in the ^{13}C nmr (Table 2) only a few signals have been observed. This prevents the use of the ^{13}C nmr spectrum to clarify the problem of the ^1H nmr spectrum (Table 1), particularly the very broad signal of the C_7H proton of the "enol/OH" tautomer. Either slow enol/enol tautomerism or the presence of a third tautomer could explain this observation.

Structure and Tautomerism of 4-Pyrazolylpyrazolinones. **12-15**.

Since the compounds prepared in a two step procedure are identical with those obtained directly from DHAA, only structures **4** and **5** (Scheme 1) ought to be considered. The proof that they have structure **4**, *i.e.* 1-R^2-3-methyl-5-hydroxypyrazolylpyrazoles results from the nmr study.

From the ^1H nmr spectra (Table 1) it can be noted that the signal of the 3'-methyl group is rather insensitive to the solvent, 2.40 ppm in deuteriochloroform and 2.30 ppm in DMSO-d_6, and also that no coupling is observed between this methyl and proton H-4'. Both facts are characteristic of a methyl group in position 3 of the pyrazole ring [8]. A methyl group in position 5, structure **5**, would show solvent dependence of its chemical shift and a small coupling (≃ 0.7 Hz) with H-4'. Another proof of structure **4** is the "non planarity" of the *p*-chlorophenyl in position 1' (R^2), compounds **12** and **14**, compared with the "planarity" (in the sense of a lower torsional angle) of the same group in position 1 (R^1), compounds **12** and **13**. The difference in chemical shifts of the *ortho* and *meta* protons is 0.26 ppm in DMSO-d_6 and 0.47 ppm in deuteriochloroform for "planar" *p*-chlorophenyl groups and about 0.02 ppm (DMSO-d_6 and deuteriochloroform) for twisted *p*-chlorophenyl groups (Table 1), which is consistent with a known rule of arylpyrazoles [8]. The twisted *p*-chlorophenyl group in position 1' shields the opposite 3-methyl group.



12

The ^{13}C nmr data (Table 2) confirms these findings. The 3'-methyl group resonates at about 13.4 ppm which is typical of a 3-methylpyrazole [4,9]. Moreover, Begtrup [10] has

devised two rules to determine if an *N*-phenyl group is "planar" or "twisted" in 1-phenylazoles: (i) $\delta C_o \simeq 119$ ppm if planar and $\simeq 125$ ppm if twisted; (ii) $\Delta\delta = \delta C_m - \delta C_o \simeq 10$ ppm if planar and 4 ppm if twisted. In compound **12**, the planar 1-*p*-chlorophenyl group has $\delta C_o = 121.6$ ppm and $\Delta\delta = 7.3$ ppm whereas the twisted 1'-*p*-chlorophenyl group has $\delta C_o = 124.8$ ppm and $\Delta\delta = 4.0$ ppm.

The angle between the 4'-phenyl group and the thiazolyl ring is the same in position 1 (**14**, $\Delta\delta = 2.7$ ppm; **15**, $\Delta\delta = 2.9$ ppm) than in position 1' (**13**, $\Delta\delta = 2.9$ ppm; **15**, $\Delta\delta = 2.4$ ppm). This $\Delta\delta$ value has been found for other non sterically hindered phenylthiazoles ($\Delta\delta = 2.6$ ppm [11]) and shows that the phenyl ring is too far apart from the pyrazole ring to be sensitive to steric effects.

Conclusions.

The reaction between *p*-chlorophenyl- and 4-phenylthiazol-2-ylhydrazine and dehydroacetic acid yields a single compound for which structure **4** has been established. The compound, both in deuteriochloroform and in hexadeuteriodimethyl sulfoxide exists as the OH tautomer without observable signals belonging to the CH tautomer. The pyrazolyl group at position 4 shifts the equilibrium towards the aromatic tautomer, a fact consistent with previous literature results [2].

EXPERIMENTAL

Melting points were measured in open capillaries and are uncorrected. The ir spectra (in nujol) were recorded on a Beckman IR-20 spectrophotometer. The ^1H nmr spectra were recorded at 293 K on a Bruker AM-200 instrument operating at 200 MHz using TMS as internal standard. The ^{13}C nmr spectra were recorded on a Bruker AM-200 operating at 50 MHz. Mass spectra were run on a JEOL JMS D-3005 instrument equipped with data analyzer JEC 980B.

1-(*p*-Chlorophenyl)-3-methyl-5-hydroxypyrazole **8**.

To a solution of *p*-chlorophenylhydrazine (0.01 mole) in ethanol (60 ml) ethyl acetoacetate (0.01 mole) and a few drops of hydrochloric acid was added. The reaction mixture was refluxed for 4 hours, the volume reduced and the separated solid was filtered, washed, dried and crystallized from ethanol, yield (70%), mp 172° (Lit [12] 172°).

1-(4-Phenyl-2-thiazolyl)-3-methyl-5-hydroxypyrazole **9**.

It was similarly prepared and crystallized from ethanol, mp 192° (Lit [13] 189°, Lit [14] 196°).

1-(*p*-Chlorophenyl)-3-methyl-4-(acetylacetyl)-5-hydroxypyrazole **10**.

This synthesis proceeds in two steps. In the first one, a mixture of *p*-chlorophenylhydrazine (0.001 mole) and DHAA (0.001 mole) in benzene was refluxed for 5 minutes on a water bath. The yellow solid which separated out during refluxing, was filtered, washed and crystallized from ethanol to yield 90% of 3-acetyl-4-hydroxy-6-methyl-2*H*-pyran-2-[(*p*-chlorophenyl)hydrazone], mp 186°; ir: ν NH 3440, ν CO 1680 cm^{-1}; pmr (TFA): δ 2.50 (1, 3H, pyrone-6-CH_3), 3.10 (s, 3H, CH_3), 6.64 (s, 1H, pyrone-5-*H*), 7.02 (d, 2H, J = 7 Hz, Ar-*H*), 7.41 (d, 2H, J = 7 Hz, Ar-*H*).

Anal. Calcd. for $C_{14}H_{13}ClN_2O_3$: C, 57.43; N, 9.57. Found: C, 57.64; N, 9.24.

In the second step, the *p*-chlorophenylhydrazone of DHAA thus obtained (0.001 mole) was refluxed in a solution of acetic acid-ethanol (3:2) for 2 hours. A yellow solid obtained after evaporating the solvent was crystallized from ethanol, yield 80%, mp 150°; ir: ν CO 1620 cm^{-1}; ms: (m/e) 292/294 (M^+).

Anal. Calcd. for $C_{14}H_{13}ClN_2O_3$: C, 57.43; N, 9.57. Found: C, 57.13; N, 9.26.

1-(4-Phenyl-2-thiazolyl)-3-methyl-4-(acetylacetyl)-5-hydroxypyrazole **11**.

This synthesis was performed through a modified procedure involving the Hantzsch thiazole synthesis [15].

Thiosemicarbazone of DHAA [16] (0.01 mole) was suspened in absolute ethanol having anhydrous sodium acetate (0.01 mole). Phenacyl bromide (0.01 mole) was subsequently added with stirring and the reaction mixture was refluxed for 30 minutes. The yellow solid which separated out during refluxing was filtered washed with a little hot ethanol and crystallized from ethanol to yield 74% of 3-acetyl-4-hydroxy-6-methyl-2*H*-pyran-2-[(4-phenyl-2-thiazolyl)hydrazone], mp 173°; ir: ν NH, OH 3400-3100, CO 1680 cm^{-1}; pmr (TFA): δ 2.40 (s, 3H, pyrone-C_6-CH_3), 2.87 (s, 3H, CH_3), 6.38 (s, 1H, pyrone-5-*H*), 7.05 (s, 1H, thiazol-5-*H*), 7.40-7.70 (m, 5H, Ar-*H*); ms: (m/e) 341 (M^+).

Anal. Calcd. for $C_{17}H_{15}N_3O_3S$: C, 59.82; N, 12.31. Found: C, 59.64; N, 11.92.

The hydrazone thus obtained was refluxed in a solution of acetic and ethanol (1:1) for 2 hours. The solid was fitered and crystallized from ethanol, yield 59%, mp 145°; ir: ν OH 3500-3200, CO 1700 cm^{-1}; ms: (m/e) 341 (M^+).

Anal. Calcd. for $C_{17}H_{15}N_3O_3S$: C, 59.82; N, 12.31. Found: C, 59.92; N, 11.92.

1,1'-(Di-*p*-chlorophenyl)-3,3'-dimethyl-5-hydroxy[4,5'-bipyrazol] **12**.

To an ethanolic solution (20 ml) of **10** (0.001 mole) *p*-chlorophenylhydrazine (0.001 mole) was added. After refluxing for 30 minutes, six drops of hydrochloric acid were added and refluxing was continued for another 2 hours. A solid which separated out on cooling, was filtered, washed with ethanol and dried, yield 68%, mp 286°.

Anal. Calcd. for $C_{20}H_{16}Cl_2N_4O$: C, 61.15; N, 14.04. Found: C, 61.38; N, 13.90.

Compound **13** was similarly prepared by treating **10** with 4-phenylthiazol-2-yl-hydrazine, yield 61%, mp 258°.

Anal. Calcd. for $C_{23}H_{18}ClN_5OS$: C, 61.67; N, 15.64. Found: C, 61.50; N, 15.48.

3,3'-Dimethyl-1,1'-bis(4-phenyl-2-thiazolyl)-5-hydroxy[4,5'-bipyrazol] **15**.

An ethanolic solution (20 ml) of **11** (0.001 mole) and 4-phenylthiazol-2-yl-hydrazine (0.001 mole) was refluxed for 30 minutes then, six drops of hydrochloric acid were added and refluxing was continued for 2 hours. The precipitated solid was filtered, washed with ethanol and dried, yield 58%, mp 250°; ir: OH 3600-3280 cm^{-1}; ms: (m/e) 496 (M^+).

Anal. Calcd. for $C_{26}H_{20}N_6OS_2$: C, 62.90; N, 16.93. Found: C, 62.64; N, 17.24.

Compound **14** was similarly prepared by treating **11** with *p*-chlorophenylhydrazine, yield 63%, mp 296°.

Anal. Calcd. for $C_{23}H_{16}ClN_5OS$: C, 61.67; N, 15.64. Found: C, 61.51; N, 15.42.

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