Synthesis of Acetylenic β-Diketones and Their Conversion into 4*H*-Pyran-4-ones, Pyrazoles, and 1-Hydroxy-4-pyridones

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A simple method for the synthesis of acetylenic β-diketones is described. They can be cyclized to the corresponding 4*H*-pyran-4-ones with acids. Their reaction with hydrazine hydrate gave pyrazole derivatives isomeric with those obtained from 4*H*-pyran-4-ones. With hydroxylamine hydrochloride in ethanol, 1-hydroxy-4-pyridones are formed.

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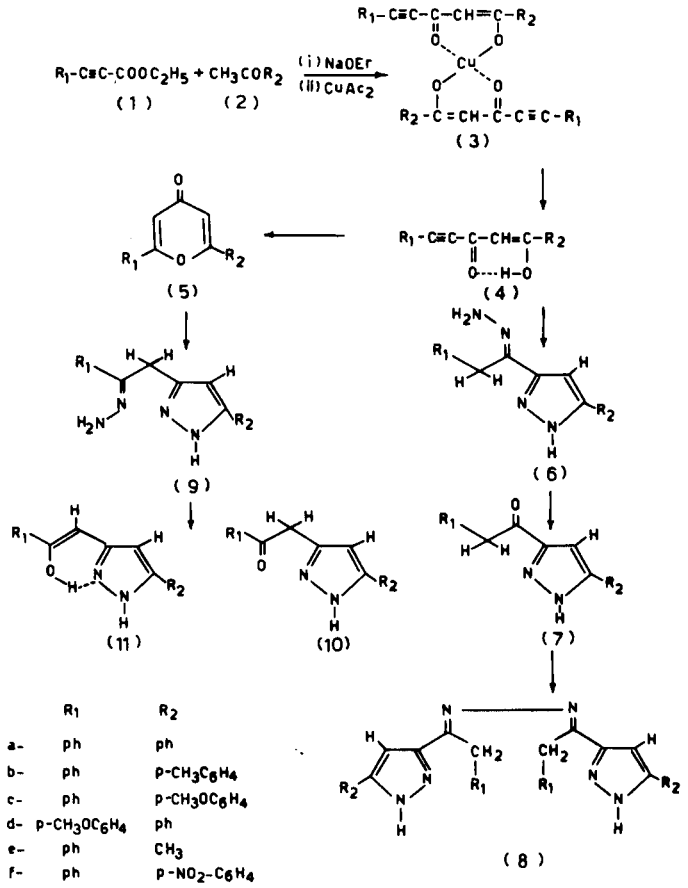
While the chemistry of diacetylenic ketones have received considerable attention (1), the equally important acetylenic β-diketones have been reported less in the literature probably due to the difficulties encountered in their syntheses. One of the methods attempted for the synthesis of these compounds involves the base catalysed Claisen condensation of acetylenic esters with ketones. However, these reactions generally lead to 4*H*-pyran-4-one derivatives due to the susceptibility of the acetylenic β-diketones to cyclization under the reaction conditions. Nevertheless, in some cases (2) it was possible to isolate these compounds alongside the pyrones. In an earlier publication (3), the reaction of ethyl phenylpropiolate with *p*-methyl- and *p*-methoxyacetophenones was reported to give 2-*p*-tolyl- and 2-*p*-methoxyphenyl-6-phenyl-4*H*-pyran-4-ones, respectively. Two other products were also isolated which were considered to be the acetylenic β-diketones **4b** and **4c**, respectively. However, spectral characteristics of these products were not consistent with the above assignment. In the present work, a simple method is described for the synthesis of acetylenic β-diketones and some of their reactions are investigated.

The reaction mixtures from the sodium ethoxide catalysed condensation of acetylenic esters **1** with suitable ketones **2** were treated with aqueous copper acetate, and the separated copper salts **3** were subsequently decomposed on treatment with hydrochloric acid to the corresponding 1,5-diarylpent-1-yne-3,5-diones **4a-d**.



Scheme I

The infrared spectra of these acetylenic β-diketones showed a broad absorption in the region 1600-1625 cm^{-1} characteristic of β-diketones (2), besides the acetylenic stretching band in the range 2220-2258 cm^{-1}. The chelated enolic structure **4** of these compounds is evident from their ^1H nmr spectra which exhibited a singlet at δ 6.45-6.52 for the ethylenic proton while the enolic proton is probably overlapped by the aromatic protons multiplet.

The electronic spectra of the acetylenic β-diketones **4a-d** in methanol exhibited four absorption maxima in the regions 225-233, 255-262 (sh), 295-297 and 350-366 nm. In the presence of 0.1 *M* sodium methoxide, a red shift is observed for the high wave length maximum with decrease in its intensity. Meanwhile, the band at 295-297 nm disappeared and the intensity of the absorption at 255-262 nm increased appreciably which can be attributed to the anionic species of these compounds

Similar to symmetrical and asymmetrical diacetylenic ketones (4), the acetylenic β-diketones **4a-d** could be cyclized to the corresponding 4*H*-pyran-4-ones **5a-c** on reaction with acids. It is worthy to mention that treatment of the copper salts **3e,f** with hydrochloric acid led to the direct formation of the corresponding 4*H*-pyran-4-ones **5e,f** probably due to the extreme sensitivity of the respective acetylenic diketones **4e,f** to acids.

The reaction of 1,5-diarylpent-1-yne-3,5-diones **4a-c**

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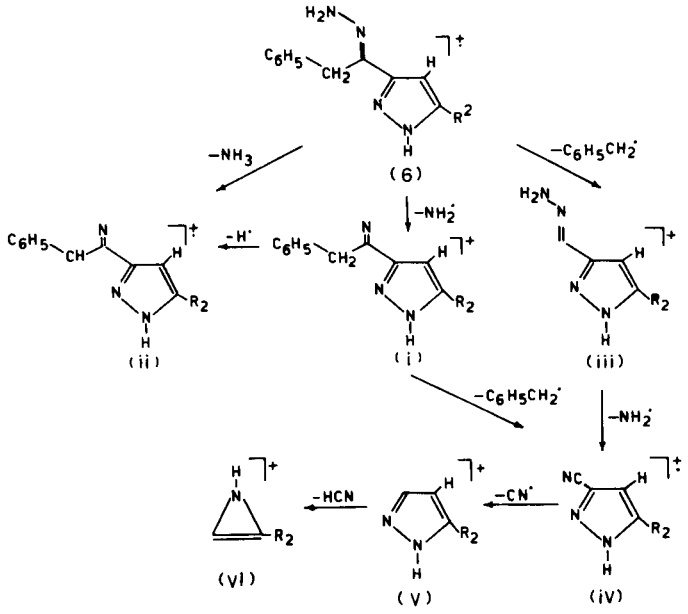
with hydrazine hydrate led to the formation of 5(3)-aryl-3(5)-[α-hydrazonophenylethyl]pyrazoles **6a-c** which could be hydrolysed into 5(3)-aryl-3(5)-phenylacetylpyrazoles **7a-c** and gave the azine derivatives **8a-c**. However, the isomeric 5(3)-phenyl-3(5)-[β-hydrazonophenylethyl]-pyrazole (**9a**) was reported (5,6) to be formed from the reaction of 2,6-diphenyl-4*H*-pyran-4-one (**5a**) or 1,5-diphenylpent-1,3,5-trione with hydrazine hydrate.

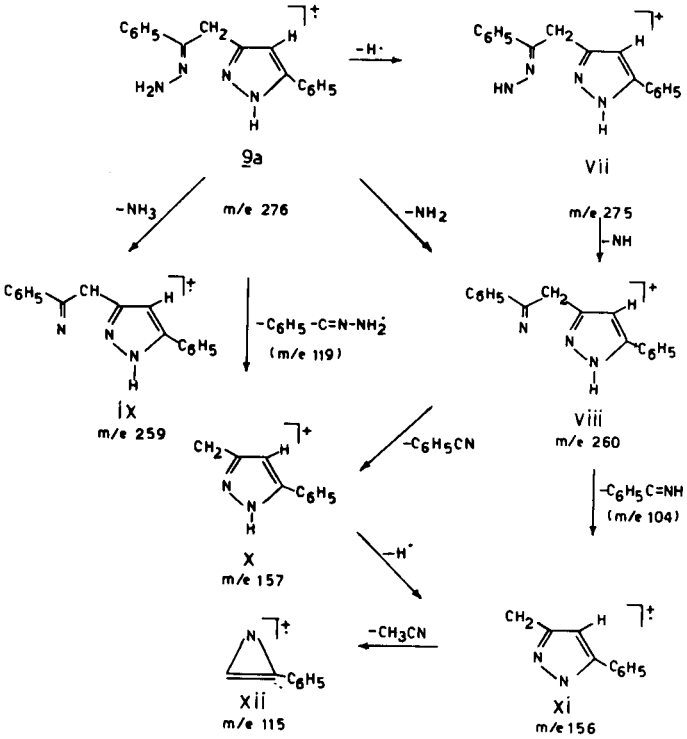
The ^{1}H nmr spectra (DMSO-d_6) of the pyrazole derivatives **6a-c** and **7a-c** exhibited, besides other characteristics, a singlet at δ 6.70-7.20 for the H-4 pyrazole ring proton. However, this signal in the spectra of the isomeric pyrazoles **9a** and **10a** appeared at higher field (δ 6.40-6.56). The observed deshielding in the former case can be related to the electron withdrawing effect of the neighbouring C=N or C-O groups.

The electronic spectra of the pyrazoles **7a-c** and **10a** exhibited a maximum absorption in the range 245-258 nm. In the presence of 0.1 *M* sodium methoxide, the spectra of **7a-c** showed an additional shoulder at 302-320 nm, while the isomeric **10a** gave a well developed maximum at 337 nm. Such difference may be ascribed to the stabilization of the enol form of the latter **11a** through hydrogen bonding.

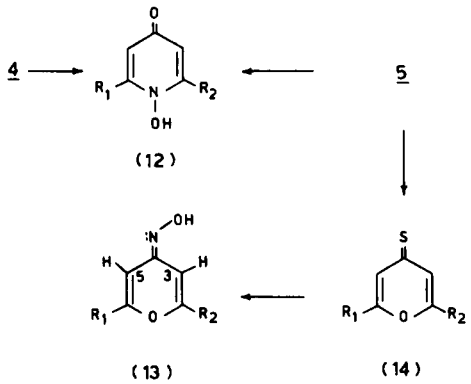
The structure of the pyrazoles **6a-c** was further confirmed from their mass spectral data. The probable structure of the common prominent peaks as well as their possible fragmentation pathways are depicted in Scheme II. It is observed that the base peaks in the spectra of these compounds are the molecular ion peaks. Elimination of NH_2 from the molecular ion gave a peak of medium intensity which may be represented as the ion *i* while the loss of ammonia molecule gave the intense peak *ii*. It is worthy to mention that the formation of (M-16) and (m-17) peaks is usually observed in the mass spectra of *N*-amino compounds (7). The (M-91) intense peak can be considered as the ion *iii* formed by the elimination of benzyl radical from the molecular ion. Subsequent loss of NH_2 from *iii* gave the species *iv* which may be also formed from the ion *i via* elimination of benzyl radical. Loss of CN radical from *iv* gave a peak of relatively weak abundance *v* which is converted to the azirinium cation *vi via* fission of the N-N linkage and subsequent elimination of HCN, frequently observed in the fragmentation of pyrazoles (8).



Scheme II



Scheme III



Scheme IV

On the other hand, the isomeric pyrazole **9a** gave a different fragmentation pattern (Scheme III). The species at m/e 260 (*viii*) may be formed from the molecular ion by loss of NH_2 radical. However, the presence of intense (55%) M-1 peak (*vii*) suggests that the formation of *viii* can be the result of a successive loss of proton and a neutral nitrine fragment (NH) from the molecular ion. Subsequent elimination of proton from *viii* gives rise to the species *ix* at m/e 259 which may be formed directly from the molecular ion by loss of ammonia molecule. Elimination of benzonitrile molecule from *viii* gave the ion *x* at m/e 157 which is also formed by the loss of $C_6H_5C{=}N\text{-}NH_2$ radical (m/e 119) from the molecular ion. Loss of proton from *x* gives the species *xi* at m/e 156 which affords the azirinium species *xii via* fission of the N-N pyrazole linkage and elimination of acetonitrile molecule.

The mass spectra of 5(3)-aryl-3(5)-phenylacetylpyrazoles **7a-c** gave a medium intensity molecular ion peaks while the base peaks are the (M-91) ions corresponding to the loss of benzyl radical from the molecular ion. However, the base peak in the spectrum of the isomeric 5(3)-phenyl-3(5)-phenacylpyrazole (**10a**) was the benzoyl radical (m/e 105).

The reaction of acetylenic ketones with hydroxylamine generally leads to isoxazole derivatives (9) while with diacetylenic ketones Δ^{-2}-isoxazolines are formed (10). In the present work the reaction of the acetylenic β-diketones **4a-c** with hydroxylamine in ethanol afforded 2,6-diaryl-1-hydroxy-4-pyridones **12a-c** which were also formed from the 4*H*-pyran-4-ones **5a-c** and hydroxylamine (3,6). The infrared spectra of these pyridones exhibited two bands in the regions 1640-1644 and 1583-1610 cm^{-1} which can be considered as coupled C=O and C=C modes (11) as well as a broad absorption in the region 3394-3554 cm^{-1} due to the OH stretching. Their electronic spectra in methanol showed a maximum absorption at 254-256 nm besides a shoulder at 305-315 nm. In the presence of 0.1 *M* sulfuric acid, the shoulder disappeared with the formation of a new absorption maximum at 345-365 nm which may be due to the protonated pyridone species.

The ^1H nmr spectra of the above pyridones (DMSO-d_6) exhibited a singlet of two protons intensity at δ 6.90-7.32 for the H-3 and H-5 pyridone ring protons, besides an exchangeable signal at δ 11.43 for the N-OH proton. However, the ^1H nmr spectra of the isomeric 4*H*-pyran-4-one oximes **13a-c**, prepared from the 4*H*-pyran-4-thiones **14a-c** and hydroxylamine (12), showed two doublets (J = 2.0 Hz) at δ 6.56-6.60 and 6.90-6.93 for the H-3 and H-5 protons, respectively. The non-equivalence of the two ring protons in the latter case is expected since the H-5 proton lies in the deshielding field of the nitrogen lone pair of electrons of the oxime residue.

It is observed that the H-3 and H-5 protons of the 4*H*-pyran-4-thiones **14a-c** resonated at much lower field relative to the analogous 4*H*-pyran-4-ones **5a-c**. Similar down-field shifts were observed for other 4*H*-pyran-4-thiones (13) as well as for the H-3 proton of 2*H*-pyran-2-thiones (14). Such significant deshielding of the α-vinylic protons in 4*H*-pyran-4-thiones is attributed to the increased magnetic anisotropy of the thione over carbonyl.

EXPERIMENTAL

Microanalyses were performed by Microanalysis Unit, Cairo University, Cairo. Infrared spectra were measured with a Unicam SP 200 spectrophotometer for potassium bromide pellets or in Nujol and electronic spectra were measured with a Unicam SP 800 spectrophotometer. The ^1H nmr spectra were recorded on a

Table 1

Analytical Data of Acetylenic β-Diketones and Pyrazole Derivatives

Compound	M.p. °C	Formula	Calcd. % C	Calcd. % H	Calcd. % N	Found % C	Found % H	Found % N
4a	95	$C_{17}H_{12}O_2$	82.3	4.8		82.6	4.8	
4b	110	$C_{18}H_{14}O_2$	82.5	5.3		82.5	5.1	
4c	112	$C_{18}H_{14}O_3$	77.7	5.0		77.6	4.8	
4d	85 (a)	$C_{18}H_{14}O_3$	77.7	5.0		77.5	4.7	
6a	196 (b)	$C_{17}H_{16}N_4$	74.0	5.7	20.2	73.5	5.4	19.9
6b	193	$C_{18}H_{18}N_4$	74.5	6.2	19.3	74.8	6.5	19.2
6c	160	$C_{18}H_{18}N_4O$	70.6	5.9	18.3	70.3	5.6	18.4
7a	187 (c)	$C_{17}H_{14}N_2O$	77.9	5.3	10.7	77.5	5.4	10.5
7b	220	$C_{18}H_{16}N_2O$	77.9	6.5	10.0	77.8	6.2	9.7
7c	205	$C_{18}H_{16}N_2O_2$	73.9	5.5	9.5	73.7	5.6	9.2
8a	225 (d)	$C_{34}H_{28}N_6$	78.5	5.4	16.2	78.5	5.7	16.0
8b	242	$C_{36}H_{32}N_6$	78.8	5.9	15.2	78.5	6.2	14.9
8c	215	$C_{36}H_{32}N_6O$	74.5	5.5	14.4	74.7	5.8	14.1

(a) Crystallized from ether. (b) Reference (10), m.p. 197-200°. (c) Reference (10), m.p. 189-191°. (d) Reference (10), m.p. 230°.

Table II

Spectral Data of Acetylenic β-Diketones

	Ir (cm^{-1})		Uv λ max, nm, (ε)				^1H nmr, δ, (Detuteriochloroform)		
	C=O	C≡C					=CH (s)	ArH (m)	others (s)
4a	1600	2220	neutral (a)	225* (11151)	255* (9257)	296 (10730)	350 (25668)	6.52	7.7	
			anionic (b)		255 (15569)		364 (18515)			
4b	1620	2258	neutral	227 (10617)	260* (9055)	295 (10461)	351 (24043)	6.50	7.6	2.24 (CH_3)
			anionic		263 (15769)		360 (20453)			
4c	1604	2220	neutral	226 (11643)	262* (8519)	296 (10649)	354 (23845)	6.48	7.5	3.88 (OCH_3)
			anionic		267 (15618)		360 (21866)			
4d	1603	2220	neutral	233 (10704)	252 (10704)	297 (8563)	366 (28364)	6.45	7.4	3.80 (OCH_3)
			anionic		279 (12577)		366 (23013)			

*Shoulder. s: Singlet. m: Multiplet. (a) Spectra carried out in methanol. (b) Spectra carried our in methanolic 0.1 *M* sodium methoxide.

Varian T-60 and Jeol 100 spectrometers with TMS as internal standard. Mass spectra were recorded on LKB 9000 instrument.

Preparation of 1,5-Diarylpent-1-yne-3,5-diones **4** (Tables I, II).

An ethereal solution of the ketone **2** (0.0287 mole) and the acetylenic ester **1** (0.0287 mole) were successively added to an ice-cold suspension of sodium ethoxide (1.95 g., 0.0287 mole) in dry ether (150 ml.). The reaction mixture was kept at 0° for 8 hours and then poured into 5% aqueous ice-cold copper acetate solution (100 ml.). The precipitated copper salt **3** was filtered, washed with ether and dried. A suspension of the crude copper salt in ether (100 ml.) was shaken with 4% hydrochloric acid (400 ml.) for 30 minutes. The ethereal solution after washing with 10% sodium bicarbonate, drying (sodium sulfate) and evaporation afforded the acetylenic β-diketone **4** (50-60% yield) which crystallized from methanol in needles.

Copper Salt of 1,5-Diphenylpent-1-yne-3,5-dione (**3a**).

A warm solution of copper acetate (0.2 g., 0.001 mole) in 90% ethanol (15 ml.) was added with stirring to a warm solution of **4a** (0.5 g., 0.020 mole) in ethanol (10 ml.). After refluxing for 15 minutes, the precipitated copper salt **3a** (40% yield) was filtered, washed with ethanol and dried, m.p. 175° dec.; ν max (cm^{-1}): 1600 (CO), 2258 (C≡C).

Anal. Calcd. for $C_{34}H_{22}O_4Cu$: Cu, 11.4. Found: Cu, 11.3.

2-*p*-Nitrophenyl-6-phenyl-4*H*-pyran-4-one (**5f**).

Decompositon of the crude copper salt **3f** with 5% hydrochloric acid led to the formation of **5f** (25% yield) which crystallized from benzene in needles, m.p. 212° dec.; ν max (cm^{-1}): 1608, 1655 (CO); uv λ max (saturated solution in methanol): 270, 200 sh nm.

Anal. Calcd. for $C_{17}H_{11}NO_4$: C, 69.6; H, 3.8; N, 4.8. Found: C, 69.3; H, 3.7; N, 4.5.

Similarly, the reaction of the copper salt **3e** with 5% hydrochloric acid afforded 2-methyl-6-phenyl-4*H*-pyran-4-one (**5e**), m.p. 88° [Lit. (15) 87-88°].

Action of Hydrochloric Acid on the Acetylenic β-Diketones.

A solution of the acetylenic β-diketone **4a-d** (0.0012 mole) in methanol (10 ml.) was refluxed with concentrated hydrochloric acid (1 ml.) for one hour. After concentration and cooling, the respective 4*H*-pyran-4-one **5a-c** (70% yield) separated out.

5(3)-Aryl-3(5)-[α-hydrazonophenylethyl]pyrazoles **6a-c** (Tables I, III, IV).

A suspension of **4a-c** (0.002 mole) in ethanol (12 ml.) was kept at 20° with 99% hydrazine hydrate (1 ml., 0.02 mole) overnight with frequent shaking and then the reaction mixture was poured into water. The separated pyrazoles **6a-c** (25-35% yield) were crystallized from benzene-petroleum ether (b.p. 60-80°) in needles; ms: m/e (relative abundance) **6a**: M^+ 276 (100), 275 (4), 260 (10), 259 (35), 230 (10), 185 (30), 169 (15), 143 (3), 116 (7), 115 (11), 104 (5), 91 (22), 90 (6), 77 (16), 65 (8); **6b**: M^+ 290 (100), 289 (5), 274 (16), 273 (57), 245 (6), 244 (22), 230 (8), 200 (7), 199 (40), 184 (6), 183 (23), 182 (14), 157 (5), 155 (9), 130 (12), 129 (14), 128 (9), 118 (9), 116 (9), 115 (12), 103 (7), 91 (46), 90 (12), 77 (12), 65 (19); **6c**: M^+ 306 (100), 292 (7), 290 (12), 289 (42), 274 (10), 260 (7), 246 (8), 215 (22), 200 (9), 199 (31), 184 (12), 173 (3), 156 (13), 146 (4), 145 (8), 134 (7), 115 (7), 102 (7), 91 (34), 90 (8), 77 (11), 65 (10); **9a**: M^+ 276 (100), 275 (55), 260 (8), 259 (22), 158 (6), 157 (11), 156 (13), 128 (12), 127 (8), 119 (82), 115 (6), 104 (16), 103 (13), 102 (7), 77 (72).

5(3)-Aryl-3(5)-phenylacetylpyrazoles **7a-c** (Tables I, III, IV).

A solution of **6a-c** (0.0011 mole) in 60% aqueous ethanol (20 ml.) was refluxed with concentrated hydrochloric acid (1 ml.)

Table III

Infrared and Electronic Spectra of Pyrazole Derivatives

	Ir (cm^{-1})					Uv λ max, nm, (ε)		
	NH_2	C=N (hydrazone)	C=N (pyrazole)	NH (pyrazole)	C=O			
6a	3250, 3430	1630	1603			neutral (a)	257 (24184)	
6b	3290, 3430	1625	1603			neutral	257 (27221)	
6c	3285, 3425	1645	1610			neutral	265 (27731)	
9a	3200, 3390	1632	1610			neutral	256 (21377)	
7a			1590	3225	1670	neutral	245 (66886)	
						anionic (b)	260 (66886)	305* (22295)
7b			1625	3290	1670	neutral	250 (18667)	
						anionic	265 (19957)	312* (6652)
7c			1615	3285	1665	neutral	258 (24360)	
						anionic	265 (25579)	320* (5075)
10a			1590	3350	1675	neutral	248 (19345)	
						anionic	250 (20492)	337 (10492)
8a		1613		3250		neutral (c)	252	295*
8b		1600		3245		neutral (c)	253	310*
8c		1600		3200		neutral (c)	262	295*

*Shoulder. (a) Spectra carried out in methanol. (b) Spectra carried out in methanolic 0.1 *M* sodium methoxide. (c) Saturated solution.

Table IV

^1H Nmr Spectral Data of Pyrazole Derivatives in DMSO-d_6

	Chemical Shift (δ/ppm)					
	CH_2 (s, 2H)	H-4 (s, 1H)	NH_2 (s, 2H)	NH (s, 1H)	ArH (m)	Others (s)
6a	4.01	6.82	6.55	12.87	7.45	
6b	4.05	6.80	6.53		7.50	2.31 (3H, CH_3)
6c	4.00	6.70	6.46	12.77	7.30	3.75 (3H, OCH_3)
9a	3.96	6.40	6.74	12.88	7.53	
7a	4.32	(a)			7.50	
7b	4.30	7.20			7.60	2.33 (3H, CH_3)
7c	4.35	6.98			7.50	3.73 (3H, OCH_3)
10a	4.40	6.56			7.69	

s: Singlet. m: Multiplet. (a) The H-4 signal is overlapped by the aromatic protons multiplet.

Table V

Infrared and Electronic Spectra of 1-Hydroxy-4-pyridones and 4*H*-Pyran-4-one Oximes

	Ir (cm^{-1}) C=C and C=O	C=N	OH		Uv λ max, nm, (ε)	
12a	1644, 1589		3394-3554	neutral (a)	254 (17721)	305* (9114)
				cationic (b)	260 (18227)	343 (6076)
12b	1643, 1583		3445	neutral	258 (18718)	306* (9844)
				cationic	262 (17886)	350 (8319)
12c	1640, 1610		3400-3500	neutral	266 (23424)	314* (9981)
				cationic	266 (19758)	366 (8555)
13a		1660	3100-3300	neutral	270 (20594)	308 (14537)
				cationic	257 (17364)	310 (31901)
13b		1659	3050-3250	neutral	276 (23398)	310* (15310)
				cationic	263 (17332)	317 (32930)
13c		1660	3050-3220	neutral	287 (27015)	320* (16595)
				cationic	274* (19296)	330 (29330)

*Shoulder. (a) Spectra carried out in methanol. (b) Spectra carried out in methanolic 0.1 *M* sulfuric acid.

Table VI

^{1}H Nmr Spectral Data of 1-Hydroxy-4-pyridones, 4*H*-Pyran-4-one Oximes, 4*H*-Pyran-4-ones and 4*H*-Pyran-4-thiones

	Solvent	Chemical Shift (δ/ppm) H-3	H-5	OH (s)	ArH (m)	Others (s)
12a	DMSO-d_6	6.90 (s, 2H)		11.43	7.70	
12b	DMSO-d_6	7.32 (s, 2H)			7.62	2.28 (3H, CH_3)
13a	DMSO-d_6	6.60 (d, 1H)	6.93 (d, 1H)	10.30	7.60	
13b	DMSO-d_6	6.60 (d, 1H)	6.92 (d, 1H)	10.30	7.50	2.22 (3H, CH_3)
13c	DMSO-d_6	6.56 (d, 1H)	6.90 (d, 1H)	10.25	7.50	3.66 (3H, OCH_3)
5a	$CDCl_3$	6.92 (s, 2H)			7.60	
5b	$CDCl_3$	6.72 (s, 2H)			7.50	2.33 (3H, CH_3)
5c	$CDCl_3$	6.78 (2, 2H)			7.45	3.90 (3H, OCH_3)
14a	$CDCl_3$	(a)			7.67 (12H)	
14b	$CDCl_3$	(a)			7.60 (11H)	2.42 (3H, CH_3)
14c	$CDCl_3$	(a)			6.45 (11H)	3.87 (3H, OCH_3)

s: Singlet. m: Multiplet. d: Doublet (j = 2.0 Hz). (a) The H-3 and H-5 protons are overlapped by the aromatic protons multiplet.

for 3 hours. On dilution with water, the pyrazoles **7a-c** which separated (70% yield) were crystallized from ethanol in needles; ms: m/e (relative abundance) **7a**: M^+ 262 (44), 172 (12), 171 (100), 116 (11), 115 (5), 91 (16), 77 (8), 65 (5); **7b**: M^+ 276 (34), 186 (14), 185 (100), 130 (14), 128 (5), 91 (26), 77 (5), 65 (13); **7c**: M^+ 292 (72), 202 (13), 201 (100), 173 (14), 146 (14), 91 (18), 77 (5), 65 (6); **10a**: M^+ 262 (28), 261 (8), 234 (15), 128 (5), 106 (12), 105 (100), 77 (45).

N,N'-Di-1-(3-arylpyrazol-5-yl)-2-phenylethylidene Hydrazine **8a-c** (Tables I, III).

These compounds were prepared (40-50% yield) by refluxing a solution of **7a-c** (0.0011 mole) in methanol (10 ml.) with glacial acetic acid (0.5 ml.) for 20 minutes and crystallized from pyridine-50% aqueous methanol in yellow needles.

They were also obtained (50-60% yield) by refluxing a solution of **6a-c** (0.0011 mole) and **7a-c** (0.0011 mole) in ethanol (20 ml.) for 3 hours.

2,6-Diaryl-1-hydroxy-4-pyridones **12a-c** (Tables V, VI).

A solution of **4a-c** (0.0016 mole) in ethanol (20 ml.) was refluxed with hydroxylamine hydrochloride (0.006 mole) and sodium acetate (0.006 mole) in water (1 ml.) for 3 hours. The hydroxypyridones **12a-c** (50-60% yield) were obtained after dilution with water and crystallized from benzene or benzene-methanol in needles.

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