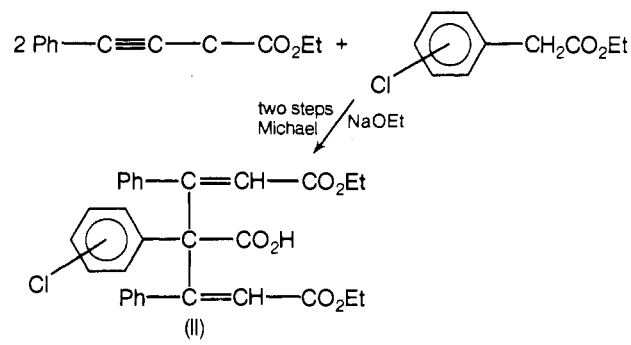
The existence of β-keto-ester in the enolic form was also supported by a positive ferric chloride test and by their formation of metal complexes.

In the case of the condensation of ethyl phenylpropiolate with ethyl *m*-chlorophenylacetate, another more crystalline compound (II) was isolated from the neutral extract. Spectral and elemental analysis agreed with the structure (II) which is the outcome of double Michael addition between 1 mole of *m*-chlorophenylacetate and 2 moles of ethyl phenylpropiolate, with subsequent hydrolysis of the acetate group as shown in Scheme 2:

Scheme 2



(II)

The presence of the carboxy-group was supported by the sodium bicarbonate test. More evidence for structure (II) was obtained from spectral data. The UV absorption spectrum showed a red shift in sodium hydroxide solution, whereas the IR spectrum showed the absence of acetylenic linkage, thus supporting the mechanism of the reaction to proceed through Michael addition. The NMR spectrum also favored the above structure. Two AB quartets appeared at 5.96 and 6.4 τ integrated to four protons. The corresponding six proton triplets appeared at 9.32 τ, thus confirming two carbethoxy groups in the molecule. The ethylenic protons of the two cinnamate fragments overlapped by the aromatic protons and showed a complex pattern between 2.52–2.9 τ. The one proton resonance signal at −1.86 τ (exchangeable with heavy water) was attributed to the carboxylic acid proton. The formation of such a compound (II) could be interpreted by certain factors including the nature of the substituent and the bulk of the molecule.

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Condensation of Acetylenic Esters with Arylacetamides

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14,5-Diaryl-1,5-dihydro-2H,6H-pyridine-2,6-dione was prepared by condensation of arylpropiolic esters with arylacetamides in the presence of powdered sodium and boiling benzene. Some of the *N*-derivatives of the condensation products were also prepared. The various structures were confirmed spectroscopically and by elemental analysis.

The condensation between ethyl phenylpropiolate and phenylacetamide (*5*) or *P*-substituted phenylacetamides (*1*) has been reported. The condensation product was identified as 4,5-diaryl-1,5-dihydro-2H,6H-pyridine-2,6-dione and not phenylpropiolyl phenylacetamide as described by Ruhemann (*9*). The reaction proceeded either by Claisen condensation of the anion $PhCH_2CO\bar{N}H$ or Michael addition of the carbanion $Ph\bar{C}HCONH_2$ to the propiolic ester with subsequent cyclization. The Claisen route seems more likely by analogy to the condensation of benzyl cyanide (*2*) or ethyl phenylacetates (*3*) with ethyl phenylpropiolate.

Experimental

Unless otherwise stated, IR spectra were measured with a Unicam SP 200 instrument for solutions in chloroform, ^1H NMR spectra with a Varian A-60 D instrument for solution in deuterated chloroform containing tetramethylsilane as internal standard, and UV spectra with a Unicam SP 800 instrument for solutions in ethanol. Microanalytical samples were analyzed in West Germany by Max Plank Institute, Ruhr. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Elemental analyses in agreement with theoretical values were obtained and submitted for review.

Condensation of arylacetamides with arylpropiolic esters. Arylacetamide (1 mole) and powdered sodium (1 gram atm) in dry benzene (150 ml) were kept under reflux for 22 hr. Arylpropiolic ester (1 mole) was then added, and heating under reflux was continued for a further 2 hr. The mixture was poured into water (200 ml), and the benzene layer was separated. The alkaline aqueous layer was acidified with dilute sulfuric acid, extracted with ether, and the ethereal extracts were shaken with sodium hydrogen carbonate solution. The nonacidic ethereal and benzene extracts were combined together and dried by sodium sulfate. The sodium hydrogen carbonate washings after acidification, extraction with ether, and evaporation gave the corresponding arylpropiolic acid.

2,5-Dimethylphenylacetamide and ethyl phenylpropiolate. 2,5-Dimethylphenylacetamide (2.8 grams), ethyl phenylpropiolate (3 grams), and powdered sodium (0.4 gram) in benzene (150 ml) were treated as described. The combined benzene–ether extracts after evaporation gave a solid (2.4

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grams). It crystallized from methanol into colorless prismatic needles of 5-(2,5-dimethylphenyl)-4-phenyl-1,5-dihydro-2H,6H-pyridine-2,6-dione (IIIa), mp 198°.

The sodium hydrogen carbonate washings after acidification, extraction with ether, and evaporation gave a solid (0.4 gram) which was mainly phenylpropiolic acid, mp and mixed mp 136°.

3,4-Dimethylphenylacetamide and ethyl phenylpropiolate. 3,4-Dimethylphenylacetamide (2.8 grams), ethyl phenylpropiolate (3 grams), and powdered sodium (0.4 gram) in benzene (150 ml) were treated as described. The combined benzene–ether extracts after evaporation gave a solid (2.7 grams). It crystallized from methanol as colorless prismatic needles of 5-(3,4-dimethylphenyl)-4-phenyl-1,5-dihydro-2H,6H-pyridine-2,6-dione (IIIb), mp 212°.

The sodium hydrogen carbonate washings after acidification, extraction with ether, and evaporation gave phenylpropiolic acid (0.5 gram), mp and mixed mp 136°.

o-Fluorophenylacetamide and ethyl phenylpropiolate. *o*-Fluorophenylacetamide (2.6 grams), ethyl phenylpropiolate (3 grams), and powdered sodium (0.4 gram) in benzene (150 ml) were treated as described. The combined benzene–ether extracts after evaporation gave a solid (2 grams). It crystallized from methanol as colorless prismatic needles of 5-*o*-fluorophenyl-4-phenyl-1,5-dihydro-2H,6H-pyridine-2,6-dione (IIIc), mp 204°.

The sodium hydrogen carbonate washings after acidification, extraction with ether, and evaporation gave phenylpropiolic acid (0.3 gram), mp 136°.

m-Fluorophenylacetamide and ethyl phenylpropiolate. *m*-Fluorophenylacetamide (2.6 grams), ethyl phenylpropiolate (3 grams), and powdered sodium (0.4 gram) in benzene (150 ml) were treated as described. The combined benzene–ether extracts after evaporation gave a solid (2.3 grams). It crystallized from methanol as colorless prismatic needles of 5-*m*-fluorophenyl-4-phenyl-1,6-dihydro-2H,6H-pyridine-2,6-dione (IIId), mp 192°.

The sodium hydrogen carbonate washings, after acidification, extraction with ether, and evaporation, gave phenylpropiolic acid (0.3 gram), mp and mixed mp 136°.

m-Chlorophenylacetamide and ethyl phenylpropiolate. *m*-Chlorophenylacetamide (2.9 grams), ethyl phenylpropiolate (3 grams), and powdered sodium (0.4 gram) in benzene (150 ml) were treated as described. The combined benzene–ether extract after evaporation gave a solid (2.5 grams). It crystallized from methanol as colorless prisms of 5-*m*-chlorophenyl-4-phenyl-1,5-dihydro-2H,6H-pyridine-2,6-dione (IIIe), mp 196°.

The sodium hydrogen carbonate washings after acidification, extraction with ether, and exaporation gave phenylpropiolic acid (0.4 gram), mp and mixed mp 136°.

Ethyl o-chlorophenylpropiolate and phenylacetamide. Phenylacetamide (2.3 grams), ethyl *o*-chlorophenylpropiolate (3.6 grams), and powdered sodium (0.4 gram) in benzene (150 ml) were treated as described. The combined benzene–ether extracts after evaporation gave a solid (2.3 grams). It crystallized from methanol as colorless prismatic crystals of 4-*o*-chlorophenyl-5-phenyl-1,5-dihydro-2H,6H-pyridine-2,6-dione (IIIf), mp 184°.

The sodium hydrogen carbonate washings after acidification gave a solid (0.3 gram) which was mainly *o*-chlorophenylpropiolic acid, mp and mixed mp 130°.

Ethyl p-chlorophenylpropiolate and phenylacetamide. Phenylacetamide (2.3 grams), ethyl *p*-chlorophenylpropiolate (3.6 grams), and powdered sodium (0.4 gram) in benzene (150 ml) were treated as described. The combined benzene–ether extracts after evaporation gave a solid (2.5 grams). It crystallized from MeOH–benzene as colorless prismatic crystals of 4-*p*-chlorophenyl-5-phenyl-1,5-dihydro-2H,6H-pyridine-2,6-dione (IIIg), mp 220°. A further 1 gram of the latter com-

Table I. 4,5-Diaryl-1-methyl-1,5-dihydro-2H,6H-pyridine-2,6-dione (IVa–h)

Compound	Mp, °C	Yield, %	Formula
IVa	118	58.2	$C_{20}H_{19}NO_2$
IVb	144	46.7	$C_{20}H_{19}NO_2$
IVc	160	70.4	$C_{18}H_{14}NO_2F$
IVd	142	53.3	$C_{18}H_{14}NO_2F$
IVe	136	81.5	$C_{18}H_{14}NO_2Cl$
IVf	136	76.9	$C_{18}H_{14}NO_2Cl$
IVh	158	95.7	$C_{19}H_{17}NO_3$

Table II. 4,5-Diaryl-1-piperidinomethyl-1,5-dihydro-2H,6H-pyridine-2,6-dione (V)

Compound	Mp, °C	Yield, %	Formula
Vb	154	50	$C_{25}H_{28}N_2O_2$
Vg	127	51.6	$C_{23}H_{23}N_2O_2Cl$
Vh	164	62.5	$C_{24}H_{26}N_2O_3$

Table III. 4,5-Diaryl-1-hydroxymethyl-1,5-dihydro-2H-pyridine-2,6-dione (VI)

Compound	Mp, °C	Yield, %	Formula
VIa	168[a]	86	$C_{20}H_{19}NO_3$
VIb	150[a]	73	$C_{20}H_{19}NO_3$
VIc	158[b]	91	$C_{18}H_{14}NO_3F$
VId	172[a]	75	$C_{18}H_{14}NO_3F$
VIe	128[a]	84	$C_{18}H_{14}NO_3Cl$
VIf	154[a]	89.5	$C_{18}H_{14}NO_3Cl$
VIg	196[b]	92	$C_{18}H_{14}NO_3Cl$
VIh	182[b]	95	$C_{19}H_{17}NO_4$

[a] Recrystallized from benzene. [b] Recrystallized from MeOH-benzene.

Table IV. UV Light Absorption Spectral Data of 4,5-Diaryl-1,5-dihydro-2H,6H-pyridine-2,6-dione (III)

	EtOH		$CHCl_3$		0.1*N* NaOH	
Compound	λ_{max}	Log ϵ_{max}	λ_{max}	Log ϵ_{max}	λ_{max}	Log ϵ_{max}
IIIa	287	4.39	293	4.24	288	4.25
	225	4.25	232	3.50	226	4.11
	221	4.29				
IIIb	288	4.53	292	4.24	290	4.07
	226	4.39	234	3.73	227	3.94
	222	4.37				
IIIc	286	4.28	292	4.16	289	4.25
	226	4.00	233	3.67	224	4.04
	220	4.07				
IIId	288	4.31	293	4.23	290	4.11
	226	4.05	232	3.69	226	3.87
	220	4.12				
IIIe	288	4.18	293	4.28	291	4.19
	221	4.07	231	3.62	227	3.99
					223	4.00
IIIf	282	3.81	286	4.03	282	3.99
	225 (sh)	3.75	234	3.73	234 (sh)	3.85
	219	3.79			226	3.90
IIIg	293	4.41	300	4.37	295	4.23
	223	4.16	234	3.58	229 (sh)	3.97
					225	4.00
IIIh	318	4.33	323	4.34	315	4.28
	230	4.02	231	3.84	231	4.03
	220	3.99				

pound was also separated during working up the reaction mixture, mp 218–20° from MeOH–benzene.

The sodium hydrogen carbonate washings after acidification, extraction with ether, and evaporation gave a solid (0.2 gram) which was mainly *p*-chlorophenylpropiolic acid, mp and mixed mp 190°.

Ethyl p-methoxyphenylpropiolate and phenylacetamide. Phenylacetamide (2.3 grams), ethyl *p*-methoxyphenylpropiolate (3.5 grams), and powdered sodium (0.4 gram) in benzene (150 ml) were treated as described. The combined benzene–ether extracts after evaporation gave a solid (4.0 grams). It crystallized from methanol as colorless prismatic crystals of 4-*p*-methoxyphenyl-5-phenyl-1,5-dihydro-2H-pyridine-2,6-dione (IIIh), mp 204°.

The sodium hydrogen carbonate washings, after acidification, extraction with ether, and evaporation, gave a solid (0.2 gram) which was mainly *p*-methoxyphenylpropiolic acid, mp and mixed mp 138°.

Action of dimethyl sulfate on 4,5-diaryl-1,5-dihydro-2H,6H-pyridine-2,6-dione (III). A solution of the imido-compound (III) (0.3 gram) in 1% sodium hydroxide solution (75 ml) was treated with dimethyl sulfate (1.5 ml). The product, which separated on cooling, crystallized from methanol as colorless needles of 4,5-diaryl-1-methyl-1,5-dihydro-2H,6H-pyridine-2,6-dione (IV) and has the following physical data (Table I).

Table V. IR and NMR Spectral Data of 4,5-Diaryl-1,5-dihydro-2H,6H-pyridine-2,6-dione (III)

Compound	IR ($CHCl_3$) Cm^{-1}	ν	τ	NMR ($CDCl_3$),[a] protons
IIIa	3500	NH	1.52	NH
	1770	C=O	2.68	ArH
	1718	C=O	2.76–3.15	
	1646	C=C	2.13 (d)	C:CH
			4.98 (d)	:CH
			7.38 (s)	ArMe
			7.86 (s)	ArMe
IIIb	3450	NH	1.48	NH
	1772	C=O	2.62–2.84	ArH
	1720	C=O	2.11 (d)	C:CH
	1650	C=C	7.78 (s)	$Ar(Me)_2$
			5.28 (d)	:CH
IIIc	3500	NH	0.82	NH
	1775	C=O	2.65	ArH
	1722	C=O	2.1 (d)	C:CH
	1650	C=C	4.78 (d)	:CH
IIId	3500	NH	1.10	NH
	1770	C=O	2.62	ArH
	1715	C=O	2.02 (d)	C:CH
	1645	C=C	5.15 (d)	:CH
IIIe	3400	NH	0.96	NH
	1765	C=O	2.62	ArH
	1718	C=O	2.03 (d)	C:CH
	1647	C=C	5.17 (d)	:CH
IIIf	3400	NH	0.98	NH
	1762	C=O	2.54–2.90	ArH
	1718	C=O	1.66 (d)	C:CH
	1640	C=C	5.5 (d)	:CH
IIIg	3280	NH	1.03	NH
	1760	C=O	2.6	ArH
	1715	C=O	2.01 (d)	C:CH
	1645	C=C	4.92 (d)	:CH
IIIh	3380	NH	1.32	NH
	1758	C=O	2.45–2.75	ArH
	1710	C=O	3.00–3.25	
	1640	C=C	2.08 (d)	C:CH
			5.18 (d)	:CH
			6.16 (s)	ArOMe

[a] NH, exchanged with D_2O and ArH, appeared as multiplet.

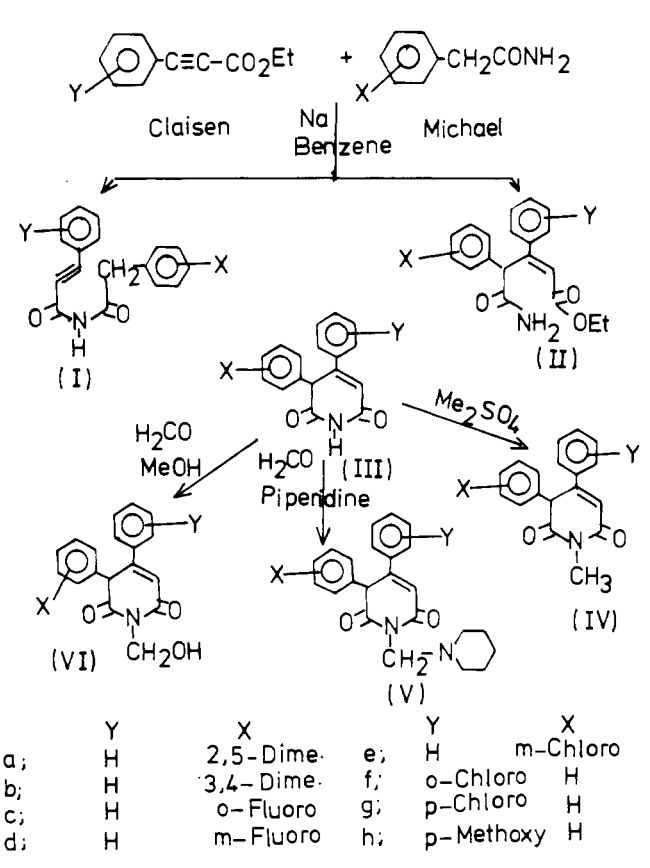
Mannich reaction (8) on 4,5-diaryl-1,5-dihydro-2H,6H-pyridine-2,6-dione (III). To a suspension of the imido-compound (III) (0.01 mole) and piperidine (0.02 mole) in methanol (30 ml), formaldehyde solution (36%, 6 ml) was added, and then the mixture was heated on a steam bath for several minutes to ensure a homogeneous mixture. The reaction mixture was kept in the ice chest overnight, and the separated solid crystallized from methanol as colorless crystals of 4,5-diaryl-1-piperidinomethyl-1,5-dihydro-2H,6H-pyridine-2,6-dione (V) and has the following physical data (Table II).

Hydroxymethylation of 4,5-diaryl-1,5-dihydro-2H-pyridine-2,6-dione (III). Formaldehyde (36%, 5 ml) was added to a suspension of the imido-compound (III) (0.5 gram) in methanol (20 ml). The mixture was heated under reflux for 3 hr and then kept in the ice chest overnight. The product, which separated after cooling, crystallized from a suitable solvent as colorless needles of 4,5-diaryl-1-hydroxymethyl-1,5-dihydro-2H,6H-pyridine-2,6-dione (VI) and has the following physical data (Table III).

Results and Discussion

In the course of our work, we were able to prepare another series of 4,5-diaryl-1,5-dihydro-2H,6H-pyridine-2,6-dione from the reaction of arylpropiolic esters with arylacetamides in the presence of sodium and boiling benzene:

(Scheme)



	Y	X		Y	X
a;	H	2,5-Dime·	e;	H	m-Chloro
b;	H	3,4-Dime·	f;	o-Chloro	H
c;	H	o-Fluoro	g;	p-Chloro	H
d;	H	m-Fluoro	h;	p-Methoxy	H

The structures of the condensation products were elucidated on the basis of their spectral analysis. The UV spectral data of these compounds (Table IV) gave good evidence for the suggested structures (III) which were comparable with the corresponding unsubstituted glutaconimides reported by Katritzky et al. (7). In an aqueous sodium hydroxide solution these compounds showed a red shift with intensification of

Table VI. IR and NMR Spectral Data of 4,5-Diaryl-1-methyl-1,5-dihydro-2H,6H-pyridine-2,6-dione (IV)

Compound	IR ($CHCl_3$) Cm^{-1}	ν	τ	NMR ($CDCl_3$),[a] protons
IVa	1760	C=O	2.68–3.25	ArH
	1700	C=O	2.1 (d)	C:CH
	1640	C=C	4.98 (d)	:CH
			6.83 (s)	NMe
			7.35 (s)	ArMe
			7.85 (s)	ArMe
IVb	1763	C=O	2.62–2.86	ArH
	1702	C=O	2.08 (d)	C:CH
	1642	C=C	5.3 (d)	:CH
			6.85 (s)	NMe
			7.8 (s)	$Ar(Me)_2$
IVc	1760	C=O	2.66–2.93	ArH
	1700	C=O	2.1 (d)	C:CH
	1645	C=C	4.84 (d)	:CH
			6.8 (s)	NMe
IVd	1765	C=O	2.6–3.00	ArH
	1710	C=O	2.00 (d)	C:CH
	1645	C=C	5.14 (d)	:CH
			6.78 (s)	NMe
IVe	1766	C=O	2.7	ArH
	1705	C=O	2.06 (d)	C:CH
	1745	C=C	5.23 (d)	:CH
			6.85 (s)	NMe
IVf	1770	C=O	2.42–2.84	ArH
	1708	C=O	1.72 (d)	C:CH
	1646	C=C	4.98 (d)	:CH
			6.82 (s)	NMe
IVg	1768	C=O	2.72	ArH
	1708	C=O	2.14 (d)	C:CH
	1648	C=C	5.28 (d)	:CH
			6.88 (s)	NMe
IVh	1755	C=O	2.6–3.3	ArH
	1696	C=O	2.14 (d)	C:CH
	1640	C=C	5.3 (d)	:CH
			6.25 (s)	ArOMe
			6.9 (s)	NMe

[a] ArH, appeared as multiplet.

Table VII. IR and NMR Spectral Data of Some 4,5-Diaryl-1-piperidinomethyl-1,5-dihydro-2H,6H,pyridine-2,6-dione (V)

Compound	IR ($CHCl_3$) Cm^{-1}	ν	τ	NMR ($CDCl_3$),[a] protons
Vb	1765	C=O	2.52–2.86	ArH
	1700	C=O	2.08 (d)	C:CH
	1640	C=C	5.27 (d)	:CH
			5.33	NCH_2N
			7.74 (s)	$Ar(Me)_2$
			7.42, 8.52	Piperidine
Vf	1763	C=O	2.54–2.84	ArH
	1700	C=O	1.64 (d)	C:CH
	1642	C=C	5.24 (d)	:CH
			5.37 (s)	NCH_2N
			7.22–7.8, 8.3–8.75	Piperidine
VIh	1750	C=O	2.56–3.24	ArH
	1696	C=O	2.1 (d)	C:CH
	1640	C=C	5.2 (d)	:CH
			5.33 (s)	NCH_2N
			6.17 (s)	ArOMe
			7.22–7.52, 8.3–8.7	Piperidine

[a] ArH, appeared as multiplet.

Table VIII. IR and NMR Spectral Data of 4,5-Diaryl-1-hydroxymethyl-1,5-dihydro-2H,6H-pyridine-2,6-dione (VI)

Compound	IR (nujol) Cm^{-1}	ν	τ	NMR ($CDCl_3$),[a] protons
VIa	3500	OH	4.8	OH
	1755	C=O	2.62–3.16	ArH
	1700	C=O	2.13 (d)	C:CH
	1640	C=C	5.02 (d)	:CH
			4.87	NCH_2O
			7.32 (s)	ArMe
			7.83 (s)	ArMe
VIb	3500	OH	4.75	OH
	1750	C=O	2.5–2.9	ArH
	1695	C=O	2.03 (d)	C:CH
	1638	C=C	5.25 (d)	:CH
			4.78	NCH_2O
			7.76 (s)	$Ar(Me)_2$
VIc	3480	OH	4.71	OH
	1755	C=O	2.5–2.97	ArH
	1696	C=O	2.08 (d)	C:CH
	1640	C=C	4.83 (d)	:CH
			4.76	NCH_2O
VId	3490	OH	4.75	OH
	1757	C=O	2.52–3.00	ArH
	1693	C=O	1.97 (d)	C:CH
	1640	C=C	5.15 (d)	:CH
			4.75	NCH_2O
VIe	3480	OH	4.73	OH
	1750	C=O	2.62	ArH
	1692	C=O	2.00 (d)	C:CH
	1638	C=C	5.2 (d)	:CH
			4.8	NCH_2O
VIf	3448	OH	4.70	OH
	1762	C=O	2.53–2.9	ArH
	1700	C=O	1.66 (d)	C:CH
	1640	C=C	5.22 (d)	:CH
			4.75	NCH_2O
VIg	3450	OH	4.25	OH
	1745	C=O	2.62	ArH
	1690	C=O	2.12 (d)	C:CH
	1635	C=C	5.2 (d)	:CH
			4.88	NCH_2O
VIh	3400	OH	4.76	OH
	1740	C=O	2.6	ArH
	1685	C=O	2.1 (d)	C:CH
	1640	C=C	5.2 (d)	:CH
			4.76	NCH_2O
			6.17 (s)	ArOMe

[a] ArH, appeared as multiplet and OH, exchanged by D_2O.

the band as compared to their absorption in ethanol (Table IV). This could be attributed to the formation of charged ionic species. The IR spectral data of these compounds (IIIa–h) (Table V) showed the absence of an acetylenic linkage, but two absorption bands appeared near 3400 and 3200 cm^{-1}, corresponding to free and bonded (N—H) stretching vibrations, respectively. Also three prominent bands between 1640–1780 cm^{-1} agreed with the presence of an unsaturated cyclic imide system (4).

The NMR spectral data (Table V) which gave good evidence for structure (III) showed the following signals: τ 5.18 (d, J 2 c/sec) characteristic of a methine proton, split by the ethylenic proton (*6*) at τ 2.08 (d, J 2 c/sec). The imido-proton showed a resonance signal around τ 1.6 (exchangeable with heavy water). A deshielding effect by halogen atoms was clearly noticed for the ethylenic proton in the imido-compound (IIIf).

The alkali-soluble imido-compound (III) was readily converted into IV by treatment with dimethyl sulfate and sodium hydroxide. The presence of the *N*-methyl group in IV was confirmed by NMR spectral data (Table VI). In all cases, it showed a signal between 6.77–6.93 τ (s), indicative of three protons.

The *N*-piperidinomethyl derivatives (V) were obtained in good yields by the action of formaldehyde and piperidine on the imido-compounds (III). The NMR spectral data (Table VII) of the *N*-piperidinomethyl derivatives showed a signal at τ 5.38 (s), indicating two protons corresponded to the deshielded (N—CH_2N) protons.

The imido-compounds (IIIa–h) were also converted into *N*-hydroxymethyl derivatives (VI) by action of formaline. The NMR spectral data (Table VIII) of compounds (VI) showed a singlet at τ 4.75 which was assigned to (N—CH_2—O) protons.

The infrared spectra of *N*-methyl, *N*-piperidinomethyl, and *N*-hydroxymethyl derivatives still showed the three-band system with a slight shift in the frequency of the bands.

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Preparation of New 2-Pyridyl and Pyrazinylhydrazones Containing Ferroin Group

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The preparation of a series of hydrazones of possible use as metal-chelating agents is described.

With the idea of providing new reagents with chelating properties for Fe (II) and Cu (I), a series of hydrazones was prepared containing the ferroin group. Among these are the previously undescribed 2-pyridylhydrazones of acetylpyrazine (*4*) (I), benzoylpyrazine (*7*) (II), 3-acetylpyridazine (*5*) (III), di(2-pyridyl)ketone (IV), and phenylglyoxal(dihydrazone) (V). Also benzoylpyrazine phenylhydrazone (VI) was prepared.

Using 2-hydrazinopyrazine, monohydrazones of the following compounds were prepared: pyridine-2-carboxaldehyde (VII), 2-acetyl (VIII) and 2-benzoyl (IX) pyridine, di(2-pyridyl)ketone (X), acetyl- (XI) and benzoyl- (XII) pyrazine, phenylglyoxal (XIII), benzil (XIV), 2,2′-pyridyl (XV), 3-acetylpyridazine (XVI), *N*-2-pyridylthiobenzamide (*1*) (XVII), *N*-2-pyridylthiopicolinamide (*3*) (XVIII), and isatin (XIX).

Dihydrazones were prepared by the action of 2-hydrazinopyrazine on 2,2′-pyridyl (XX) and phenylglyoxal (XXI). Attempts to prepare diphenyl, di(2-pyridyl) or dipyrazinyl hydrazones of 4,7-phenanthroline-5,6-quinone (XXII) resulted in each case in the formation of 5,6-dihydroxy-4,7-phenanthroline, identical with the compound prepared by the reduction of the phenanthroline quinone with Raney nickel (*2*).

$$N_2C_4H_3NHNH_2 + R_1CSNHR_2 \longrightarrow N_2C_4H_3NHN = C(R_1)—NHR_2$$

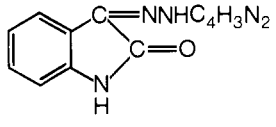
$R_1 = C_6H_5$; $R_2 = 2\text{-}C_5H_4N$ (XVII)

$R_1 = R_2 = 2\text{-}C_5H_4N$ (XVIII)

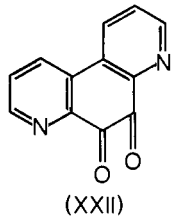
$$N_2C_4H_3NHNH_2 + R_1C(=O)—C(=O)—R_2 \longrightarrow C_4H_3N_2HN—C(R_1)=C(R_2)—NNHC_4H_3N_2$$

$R_1 = H$; $R_2 = C_6H_5$ (XIII)

$R_1 = R_2 = 2\text{-}C_5H_4N$ (XX)



(XIX)



(XXII)

Preliminary tests indicate that many of these hydrazones give a deep red color in presence of Fe (II). A detailed study of the metal-chelating properties of these compounds will be made by Alfred Schilt.

Experimental

A mixture of 0.006 moles each of 2-hydrazinopyridine or pyrazine (*6*) and carbonyl (or thiocarbonyl) compound in 25 ml of ethanol was heated at reflux for 3 hr. After evaporation of the solvent, the hydrazone was crystallized from the solvent indicated in Table I (exceptions noted in table).