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*).

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

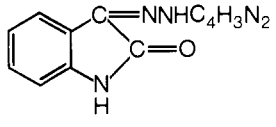
$R_1 = C_6H_5$; $R_2 = 2\text{-}C_5H_4N$ (XVII)

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

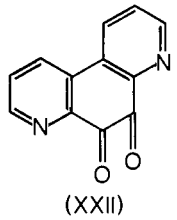
$$N_2C_4H_3NHNH_2 + R_1C(=O)—C(=O)—R_2 \longrightarrow C_4H_3N_2HN—C(R_1)=C(R_2)—NNHC_4H_3N_2$$

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

Table I. 2-Pyridyl and Pyrazinylhydrazones[a]

Hydrazone	Hydrazine	Ketone	Mp, °C	Yield	Cryst. solvent
I	Pyridyl	Acetylpyrazine	140	52.4	CH_3OH
II	Pyridyl	Benzoylpyrazine	188	29.0	CH_3OH
III	Pyridyl	3-Acetylpyridazine	137	40.0	$CH_3OH+(C_2H_5)_2O$
IV	Pyridyl	Di(2-pyridyl)ketone	140	81.2	$CH_3OH+(C_2H_5)_2O$
V	Pyridyl (2 moles)	Phenylglyoxal	225	66.7	2-Methoxyethanol
VI	Phenyl	Benzoylpyrazine	165	33.3	CH_3OH
VII	Pyrazinyl	Pyridine-2-carboxaldehyde	208	46.2	C_2H_5OH
VIII	Pyrazinyl	2-Acetylpyridine	153	37.7	CH_3OH
IX	Pyrazinyl	2-Benzoylpyridine	176	29.0	CH_3OH
X	Pyrazinyl	Di(2-pyridyl)ketone	152	36.2	CH_3OH
XI	Pyrazinyl	Acetylpyrazine	209	27.4	C_2H_5OH
XII	Pyrazinyl	Benzoylpyrazine	157	17.4	C_2H_5OH
XIII	Pyrazinyl (1 mole)	Phenylglyoxal	153	39.0	C_2H_5OH
XIV	Pyrazinyl (1 mole)	Benzil	141	21.4	CH_3OH
XV	Pyrazinyl (1 mole)	Pyridil	196	64.5	C_2H_5OH
XVI	Pyrazinyl	3-Acetylpyridazine	193	26.7	CH_3OH
XVII[b]	Pyrazinyl	*N*-2-pyridylthiobenzamide	180	50.0	C_2H_5OH
XVIII[b]	Pyrazinyl	*N*-2-pyridylthiopicolinamide	150	30.0	CH_3OH
XIX	Pyrazinyl	Isatin	313	77.6	2-Methoxyethanol
XX[c]	Pyrazinyl (1 mole)	XV	250	30.0	Aq pyridine
XXI	Pyrazinyl (2 moles)	Phenylgloxal	263	52.6	2-Methoxyethanol

[a] Elemental analyses in agreement with theoretical values were obtained and submitted for review. [b] Five hours of refluxing. [c] Five hours of heating at 150–160 without solvent.

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Generation and Reactions of Some Dimethyl Benzylphosphonate Carbanions: Synthesis of trans-Diaryl-Substituted Ethylenes

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A series of *p*-substituted benzylphosphonate carbanions is generated and reacted with a variety of substituted aromatic aldehydes to afford trans-diaryl-substituted ethylenes. In no case could the cis-isomer be isolated. The influence of substituents and solvent and base variations on the stereochemical nature of the resulting ethylenes is examined. Structural assignments of the products are based on IR and NMR spectral evidence.

The role of phosphonium ylide chemistry in the synthesis of a variety of olefinic products is widely accepted (*16, 17, 25, 26*). However, there are number of cases in which the olefin synthesis via phosphonium ylide fails because of insufficient reactivity of the latter. Recent research on the newer variation of phosphonium ylide olefination, which involves the reaction of phosphonate carbanions with carbonyl compounds (*3*), has made a significant contribution in the synthesis of sensitive olefins not preparable by ylide olefination reactions (*14, 29, 34*).

Many of the initial reports of olefin synthesis from phosphonate carbanions have shown that stereochemistry of the reaction is stereospecific and favors the formation of only the trans-isomer (*13, 14, 34*). Recently, it has been reported that in some cases this reaction is not stereospecific and a mixture of cis- and trans-isomers can be produced (*3*), the ratio of which appears to be dependent on the nature of grouping substituted on the α-carbon of the phosphonate carbanion (*30*), carbonyl compounds (*3, 5, 6, 8*), and solvent used (*10, 24*).

With the intent of examining the stereochemical pathway of the phosphonate carbanion olefination reaction, we have studied the reactions of some phosphonate carbanions (compounds 2a–e) generated from *p*-methylbenzylphosphonate (compound 1a), *p*-chlorobenzylphosphonate (compound 1b), *p*-bromobenzylphosphonate (compound 1c), *p*-iodobenzylphosphonate (compound 1d), and *p*-nitrobenzylphosphonate

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