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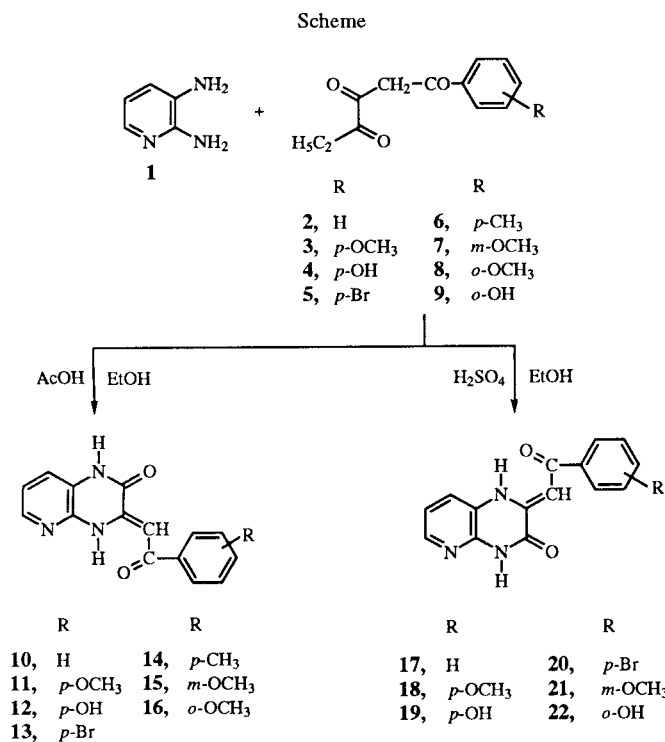
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Condensation of 2,3-diaminopyridine (1) with ethyl *o*-, *m*- and *p*-substituted benzoylpyruvates 2-9 gave two isomeric products. The preferential formation of one or the other isomer has been achieved by different reaction conditions. All the products appear to exist in the enamine form as evidenced by their ¹H nmr and ir spectra.

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When the reaction of 1 with 2-9 carried out in acetic acid solution, the main products were 3-phenacylidene-3,4-dihydro-1*H*-pyrido[2,3-*b*]pyrazin-2-ones 10-16. In order to obtain the other isomer, the reaction condition was modified, and it has been found that the same starting substances gave 2-phenacylidene-1,2-dihydro-4*H*-pyrido[2,3-*b*]pyrazin-3-ones 17-22 in aqueous sulfuric acid solution.



Both isomers exist in the enamine form in which the double bonds have been migrated onto the side chain being caused by internal hydrogen bonding. The structures are supported by their ¹H nmr and ir data (Table I). When the ¹H nmr spectra of these compounds were mea-

Table I
NMR and IR Spectral Data for Compounds 10-22

Com- pound	Side Chain (=CH) (s, 1H)	¹ H-NMR δ (ppm) Ring (=CH) at			N-H at 1 or 4 (br, 1H, 1H)	Ir (cm ⁻¹)	
		6 (dd, 1H)	7 (dd, 1H)	8 (dd, 1H)		C=O	C=C
10	6.87	8.12	7.16	7.41	12.0, 13.4	1625	1622
11	6.83	8.09	7.15	7.45	12.1, 13.3	1630	1615
12	6.80	8.09	7.15	7.42	12.0, 13.3	1620	1610
13	6.83	8.11	7.16	7.47	12.0, 13.4	1620	1605
14	6.84	8.10	7.14	7.46	12.0, 13.4	1625	1620
15	6.83	8.11	7.18	7.40	12.1, 13.3	1625	1610
16	6.86	8.13	7.18	7.40	12.0, 13.3	1630	1615
17	6.87	8.12	7.14	7.92	12.5, 13.3	1620	1615
18	6.83	8.07	7.14	7.86	12.1, 13.4	1630	1620
19	6.83	8.08	7.15	7.94	12.5, 13.3	1620	1615
20	6.79	8.11	7.16	7.93	12.5, 13.3	1625	1605
21	6.83	8.09	7.18	7.92	12.2, 13.4	1625	1615
22	6.96	8.13	7.17	7.94	12.1, 13.4	1630	1615

sured in dimethyl sulfoxide-*d*₆ (DMSO-*d*₆) with the addition of deuterium oxide, the signal of =CH did not disappear by deuterium exchange. Therefore, these compounds could probably not exist as an equilibrium mixture of the imine and enamine, but were fixed in the enamine form as shown in previous paper [1-5]. The presence of 1*H*-pyrido[2,3-*b*]pyrazin-2-one or 4*H*-pyrido[2,3-*b*]pyrazin-3-one ring in their structures is substantiated by the ¹H nmr data appearing in the literatures [6,7], respectively.

EXPERIMENTAL

Melting points are uncorrected. The ir spectra were recorded as potassium bromide disks using a Nippon Bunko IRA-1 spectrophotometer. The ¹H nmr spectra were obtained in DMSO-*d*₆ using a JEOL FX-90 spectrometer and are reported as δ values (ppm, TMS as an internal standard).

The starting material, ethyl benzoylpyruvates 2-9, were prepared according to the procedures in the literature [4,8].

Spectral data of the products 10-22 are shown in Table I.

3-Phenacylidene-3,4-dihydro-1*H*-pyrido[2,3-*b*]pyrazin-2-one (10).

Into a solution of **1** (0.66 g, 6 mmoles) in ethanol (20 ml) and 50% aqueous acetic acid (10 ml), a solution of the ethyl benzoylpyruvate (**2**) (1.32 g, 6 mmoles) in ethanol (10 ml) was added dropwise with stirring. The temperature of the reaction mixture was gradually raised to 100°. The mixture, which started to turn a deep orange with the formation of a precipitate, was refluxed for 3 hours, and then allowed to stand overnight at room temperature with continuous stirring. The crystals thus deposited were collected on a funnel and washed well with water and ethanol. The crude product was recrystallized from glacial acetic acid-ethanol, 0.98 g (59.9%), mp >300°.

Anal. Calcd. for C₁₅H₁₁N₃O₂: C, 67.92; H, 4.18; N, 15.84. Found: C, 67.65; H, 4.01; N, 16.00.

Compounds **11-16** were obtained in the same manner as described for the synthesis of **10**.

3-(*p*-Methoxyphenacylidene)-3,4-dihydro-1*H*-pyrido[2,3-*b*]pyrazin-2-one (**11**).

This compound was obtained as yellow crystals (acetic acid), yield 81%, mp 283-285°.

Anal. Calcd. for C₁₆H₁₃N₃O₃: C, 65.08; H, 4.44; N, 14.23. Found: C, 64.88; H, 4.68; N, 14.15.

3-(*p*-Hydroxyphenacylidene)-3,4-dihydro-1*H*-pyrido[2,3-*b*]pyrazin-2-one (**12**).

This compound was obtained as yellow crystals (pyridine), yield 59%, mp >300°.

Anal. Calcd. for C₁₅H₁₁N₃O₃: C, 64.05; H, 3.94; N, 14.94. Found: C, 64.32; H, 4.10; N, 15.18.

3-(*p*-Bromophenacylidene)-3,4-dihydro-1*H*-pyrido[2,3-*b*]pyrazin-2-one (**13**).

This compound was obtained as orange yellow crystals (acetic acid), yield 81%, mp >300°.

Anal. Calcd. for C₁₅H₁₀BrN₃O₂: C, 52.35; H, 2.93; N, 12.21; Br, 23.22. Found: C, 52.16; H, 3.06; N, 12.10; Br, 23.07.

3-(*p*-Methylphenacylidene)-3,4-dihydro-1*H*-pyrido[2,3-*b*]pyrazin-2-one (**14**).

This compound was obtained as orange crystals (acetic acid), yield 70%, mp >300°.

Anal. Calcd. for C₁₆H₁₃N₃O₂: C, 68.81; H, 4.69; N, 15.05. Found: C, 68.94; H, 4.80; N, 15.26.

3-(*m*-Methoxyphenacylidene)-3,4-dihydro-1*H*-pyrido[2,3-*b*]pyrazin-2-one (**15**).

This compound was obtained as yellow crystals (acetic acid), yield 61%, mp 276-278°.

Anal. Calcd. for C₁₆H₁₃N₃O₃: C, 65.08; H, 4.44; N, 14.23. Found: C, 64.98; H, 4.42; N, 14.29.

3-(*o*-Methoxyphenacylidene)-3,4-dihydro-1*H*-pyrido[2,3-*b*]pyrazin-2-one (**16**).

This compound was obtained as yellow crystals (acetic acid-ethanol), yield 70%, mp 268-270°.

Anal. Calcd. for C₁₆H₁₃N₃O₃: C, 65.08; H, 4.44; N, 14.23. Found: C, 64.98; H, 4.42; N, 14.29.

Compounds **17-22** were prepared in a manner similar to that described for the synthesis of **10** using 1*M* sulfuric acid instead of 50% acetic acid.

2-Phenacylidene-1,2-dihydro-4*H*-pyrido[2,3-*b*]pyrazin-3-one (**17**).

This compound was obtained as yellow crystals (acetic acid), yield 55%, mp >300°.

Anal. Calcd. for C₁₅H₁₁N₃O₂: C, 67.92; H, 4.18; N, 15.84. Found: C, 67.73; H, 4.11; N, 16.07.

2-(*p*-Methoxyphenacylidene)-1,2-dihydro-4*H*-pyrido[2,3-*b*]pyrazin-3-one (**18**).

This compound was obtained as yellow crystals (acetic acid), yield 60%, mp 291-293°.

Anal. Calcd. for C₁₆H₁₃N₃O₃: C, 65.08; H, 4.44; N, 14.23. Found: C, 65.23; H, 4.32; N, 14.19.

2-(*p*-Hydroxyphenacylidene)-1,2-dihydro-4*H*-pyrido[2,3-*b*]pyrazin-3-one (**19**).

This compound was obtained as yellow crystals (pyridine), yield 48%, mp >300°.

Anal. Calcd. for C₁₅H₁₁N₃O₃: C, 64.05; H, 3.94; N, 14.94. Found: C, 64.28; H, 3.86; N, 15.11.

2-(*p*-Bromophenacylidene)-1,2-dihydro-4*H*-pyrido[2,3-*b*]pyrazin-3-one (**20**).

This compound was obtained as orange yellow crystals (acetic acid), yield 46%, mp >300°.

Anal. Calcd. for C₁₅H₁₀BrN₃O₂: C, 52.35; H, 2.93; N, 12.21; Br, 23.22. Found: C, 52.09; H, 3.16; N, 12.10; Br, 23.11.

2-(*m*-Methoxyphenacylidene)-1,2-dihydro-4*H*-pyrido[2,3-*b*]pyrazin-3-one (**21**).

This compound was obtained as orange crystals (acetic acid), yield 49%, mp 274-278°.

Anal. Calcd. for C₁₆H₁₃N₃O₃: C, 65.08; H, 4.44; N, 14.23. Found: C, 64.98; H, 4.42; N, 14.29.

2-(*o*-Hydroxyphenacylidene)-1,2-dihydro-4*H*-pyrido[2,3-*b*]pyrazin-3-one (**22**).

This compound was obtained as yellow crystals (acetic acid), yield 23%, mp >300°.

Anal. Calcd. for C₁₅H₁₁N₃O₃: C, 64.05; H, 3.94; N, 14.94. Found: C, 63.88; H, 4.05; N, 14.87.

REFERENCES AND NOTES

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