REACTION OF β-CYANOMETHYLENE-β-ENAMINO DIKETONES AND -KETO ESTERS WITH HYDRAZINES: SYNTHESIS OF PYRAZOLE AND PYRIDINE DERIVATIVES

Chiara B. Vicentini, Maurizio Manfrini, Manuela Mazzanti, and Augusto C. Veronese*

Dipartimento di Scienze Farmaceutiche, via Fossato di Mortara 17, I-44100 Ferrara, Italy

Abstract - 4-Acetyl-3-amino-5-oxo-3-hexenenitrile (**1a**) reacts with hydrazines to give pyrazolyl enaminonitriles (**2**) while 2-acetyl-3-amino-4-cyano-2-butenoic acid methyl ester (**1b**) reacts with hydrazines to give pyridine derivatives (**6**) or (**7**).

β-Dicarbonyl compounds react with nitriles in the presence of catalytic amounts of metal acetylacetonates or of stoichiometric amounts of tin(IV) chloride, to give β-enamino diones, derived from C-C bond formation between the methylene and the cyano groups.[1] Such compounds can be useful intermediates in the synthesis of heterocycles,[2] as we have recently proved for the synthesis of pyrazole, isoxazole and pyrimidine *ortho*-dicarboxylic acid derivatives.[3]

β-Diketones and β-keto esters react with malononitrile in the presence of metal catalyst to give β-cyanomethyleneβ-enamino diketones or -keto esters.[4] In order to investigate the reactivity of these compounds and to study their utilization as intermediates in the synthesis of heterocycles, 4-acetyl-3-amino-5-oxo-3-hexenenitrile (**1a**) and 2-acetyl-3-amino-4-cyano-2-butenoic acid methyl ester (**1b**) have been reacted with hydrazine and aliphatic or aromatic hydrazines in ethanol or acetic acid in mild experimental conditions and in this paper we report on the results obtained.

Reaction of compound (1a) with hydrazines

The reaction of **1a** with hydrazine, methylhydrazine or ethylhydrazine in ethanol gave the 3-amino-3-pyrazolylpropenenitrile derivatives (**2a,b,c**) as the only reaction products with the yields ranging from 55 to 76% (Scheme **1**, entries 1, 3, 5).

The reaction of **1a** with phenylhydrazine in ethanol afforded two compounds corresponding to the the enaminone (**3**) and the pyrazole derivative (**4**) (entry 7).

The reaction with *p*-nitrophenylhydrazine afforded the deacetylated derivative (**5**) (entry 9). In the last two reactions acetylhydrazine derivatives were obtained in addition to compounds (**3**), (**4**) and (**5**).

When the same reactions were carried out in acetic acid compounds (**2a-e**) were obtained as the only reaction products in different yields. High yields have been obtained in the reactions with methyl- and phenylhydrazines, medium yields with *p*-nitrophenylhydrazine and low yields with hydrazine and ethylhydrazine (entries 2, 4, 6, 8, 10).

In particular the reactions of **1a** with phenyl- and *p*-nitrophenylhydrazines in acetic acid afforded compounds (**2d**) and (**2e**), not obtained in the corresponding reactions carried out in ethanol.
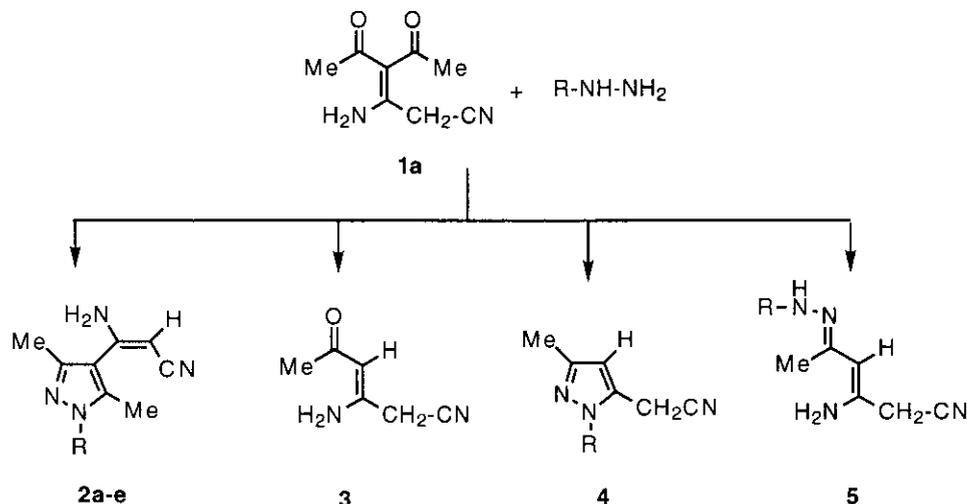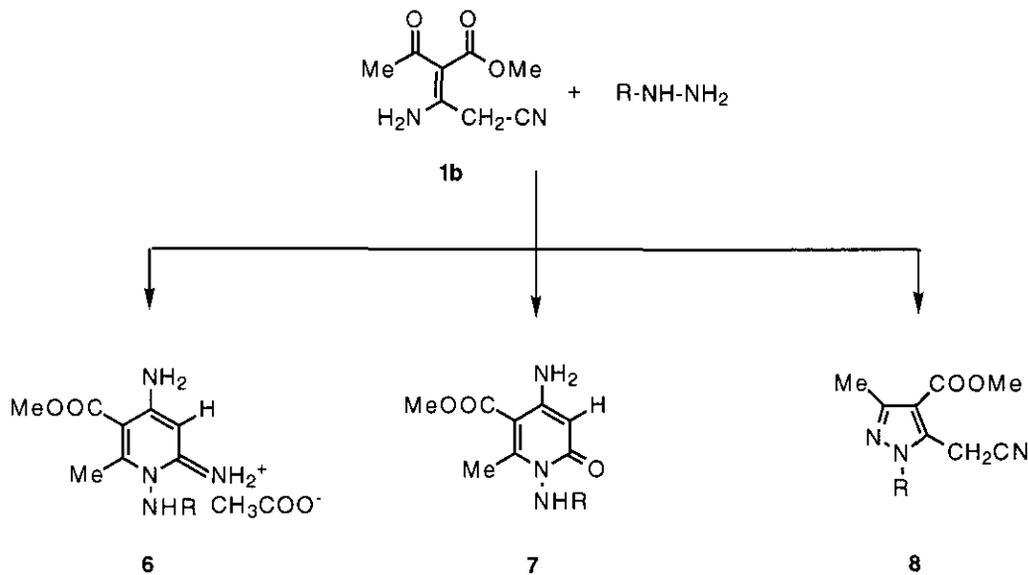

entry	R	experimental conditions	product	yields (%)
1	H	EtOH, rt, 6 h	**2a**	55
2	H	AcOH, rt, 3 d	**2a**	21
3	Me	EtOH, rt, 6 h	**2b**	76
4	Me	AcOH, rt, 3 d	**2b**	74
5	Et	EtOH, rt, 6 h	**2c**	75
6	Et	AcOH, rt, 3 d	**2c**	18
7	Ph	EtOH, rt, 3 d	**3**	24
			4	18
8	Ph	AcOH, rt, 6 h	**2d**	63
9	*p*-NO$_2$-Ph	EtOH, rt, 3 d	**5**	33
10	*p*-NO$_2$-Ph	AcOH, rt, 6 h	**2e**	48

Scheme 1

Reaction of compound (1b) with hydrazines

The reaction of **1b** with hydrazine, methyl- and phenylhydrazines in ethanol at room temperature for 3 days did not afford any derivative and only the unreacted materials were detected.

When the same reaction was carried out in acetic acid, two different kinds of derivatives were obtained. In the reaction of **1b** with hydrazine and methylhydrazine the only isolated products were the pyridinone derivatives (**7a,b**). In the reaction of **1b** with phenylhydrazine two compounds were isolated corresponding to pyridine derivative (**6**) and pyrazole derivative (**8**).

entry	R	experimental conditions	product	yields (%)
1	H	AcOH, rt, 3 d	**7a**	41
2	Me	AcOH, rt, 3 d	**7b**	41
3	Ph	ACOH, rt, 3 d	**6**	24
			8	28

Scheme 2

## Discussion

The reactions of compounds (**1**) with hydrazine, alkyl- and arylhydrazines afford different compounds depending on the nature of **1**, on the kind of hydrazine and on the solvent. The obtained results are summarized and explained in Scheme **3**.

In the reactions of **1a, b** with hydrazines the first step is the attack of one NH of hydrazines on the acetyl carbonyl group with the formation of intetermediate α,β-unsaturated hydrazino derivatives, which were never isolated. The reactions of **1a** (R'=Me) proceed generally with the subsequent attack of the second NH on the other acetyl carbonyl group with the formation of pyrazolyl enaminonitriles (**2**). This kind of reaction occurs with all hydrazines in acetic acid but only with the more reactive hydrazine and alkylhydrazines in ethanol. In the reactions of arylhydrazines carried out in ethanol the intermediates undergo a retro-Claisen reaction with the formations of compounds (**5**). This compound was isolated after purification of the reaction mixture by silica gel chromatography only for R=p-NO$_2$-Ph .

In the reaction with phenylhydrazine two compounds have been instead obtained: the enaminone (**3**), derived from the deacetylation of **1a** or alternatively from the hydrolysis of the pertinent **5** during the purification on silica gel, and the pyrazole derivative (**4**). This compound derives from the cyclisation of **5**

to **4** in a Michael type reaction due to an attack of the hydrazine NH linked to the phenyl group onto the *beta* position of unsaturated intermediate (**5**), followed by elimination of ammonia.
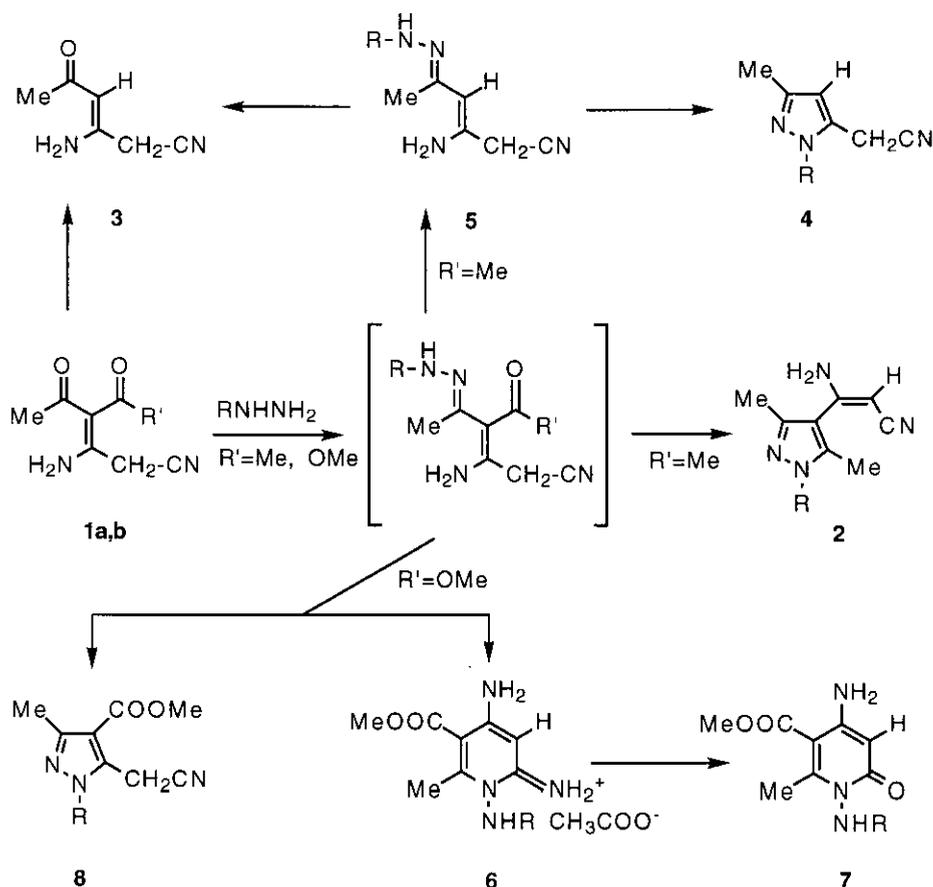
Scheme 3

The different behaviour of arylhydrazines with respect to alkylhydrazines can be due to the low nucleophilic character of the NH linked to aryl group. This group is unable to attack the second carbonyl group having the low electrophilic character of a vinylogous amide and so the reaction goes further giving, through a retro Claisen reaction, the deacylated derivative (**5**) which cyclises to pyrazole derivative (**4**). The effect of acetic acid in favoring the formation of compounds (**2**) in all the reactions can be due to the protonation of the oxygen of the second acetyl group which affords an increase of its electrophilic character.

In the reactions of **1b** (R'=OMe) with hydrazines the unsaturated hydrazino intermediates don't afford a derivative like **2** due to the low reactivity of the ester group. The reaction proceeds only when acetic acid is used as solvent generally with a second attack of hydrazino nitrogen onto the cyano group electrophilically activated by the protonation with the solvent. The 2-iminopyridine acetate (**6**) was isolated after purification by silica gel chromatography only when R=Ph while in the other reactions the 2-pyridone derivatives

(**7a,b**), derived from hydrolisis of pertinent intermediates (**6**), were obtained. In the reaction of **1b** with phenylhydrazine the pyrazole (**8**) was isolated as by-product. The formation of this compound can be explained by a mechanism involving a Michael-type reaction like that affording compound (**4**).

All the reported structures are confirmed by spectral data. In particular the structures of the two pyrazole derivatives (**4**) and (**8**) have been assigned instead of their isomeric structures on the basis of ^{13}C-NMR spectra. In both compounds the C-3 and the C-5 carbon atoms show resonances at *ca.* 150 and 136 ppm rispectively. In the coupled spectrum of **8** the C-3 resonance is a quartet with a ^{2}J of 6.7 Hz due to the coupling with the hydrogens of the vicinal methyl group while the C-5 is a triplet with a ^{2}J=7.4 Hz due to the coupling with the vicinal methylene group. A similar situation is present in the derivative (**4**), in which the C-3 carbon is a double quartet and the C-5 is a double triplet in that they are coupled respectively with the hydrogen of methyl and methylene groups but also with hydrogen linked to C-4 carbon atom.[5]

The results show that the enaminones (**1a,b**) are complex systems which show many electrophilic centers: the acetyl carbonyl groups, the *beta* position of unsaturated system and the cyano group. The reactivity of these centers with respect to hydrazines depends on nucleophylicity of hydrazine and on the reaction medium. In convenient experimental conditions the reactions of **1a,b** with hydrazines allow the formation of pyrazole and of pyridine derivatives[6] in medium to good yields.

EXPERIMENTAL

Melting points were determined in open capillary tubes on a Büchi apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer Paragon 500 FT-IR spectrophotometer (values in cm^{-1}). NMR spectra were recorded on Brucker AC (200 MHz) spectrometer. Chemical shifts are given in ppm (δ) with respect to tetramethylsilane and coupling constants (J) are in Hertz. Column chromatography was performed using Merk silica gel (70-230 mesh); for the flash chromatography technique, silica gel (230-400 mesh) was employed. Compounds (**1a,b**) were prepared according to the literature.[4]

Reaction of 1a with hydrazines

General procedures

The reaction was carried out in two different experimental conditions.

Method A: To a solution of **1a** (0.33 g, 2 mmol) in ethanol (10 mL) the pertinent hydrazine (2.2 mmol) was added. The reaction mixture was stirred at rt for 6 h, concentrated under reduced pressure to give a residue which was purified by flash column chromatography.

Method B: To a solution of **1a** (0.33 g, 2 mmol) in acetic acid (10 mL) the pertinent hydrazine (2.2 mmol) was added. The reaction mixture was stirred at rt for 6 h, concentrated under reduced pressure to give a residue which was purified by flash column chromatography.

Reactions of 1a with hydrazine hydrate

Following the *method A*, 3-amino-3-(3,5-dimethylpyrazol-4-yl)propenenitrile (**2a**) was obtained as pale yellow crystals, yield 55% (purified by flash column chromatography, eluent ethyl acetate: light petroleum 8:2), mp 187-190°C (ethyl acetate/light petroleum); IR (KBr): *3425, 3314, 3201, 2179, 1646, 1576* cm^{-1}; ^{1}H-NMR (CDCl$_3$): δ 2.17 (s, 6H, 2Me), 4.19 (s, 1H, CH), 6.45 (br s, 2H, NH$_2$), 12.41 (br s, 1H, NH). *Anal.* Calcd for C$_8$H$_{10}$N$_4$: C, 59.24; H, 6.21; N, 34.54. Found: C, 59.18; H, 6.25; N, 34.48. Following the *method B* compound (**2a**) was obtained in 21% yield.

Reactions of 1a with methylhydrazine

Following the *method A*, 3-amino-3-(1,3,5-trimethylpyrazol-4-yl)propenenitrile (**2b**) was obtained as pale yellow crystals, yield 76% (purified by flash column chromatography, eluent ethyl acetate: light petroleum 8:2), mp 171-173°C (triturated with ethyl ether); IR (KBr): 3387, 3197, 2182, 1650, 1586 cm^{-1}; ^{1}H-NMR (CDCl$_3$): two geometric isomers are present. The major isomer (85%) shows resonances at δ 2.25 (s, 3H, Me), 2.29 (s, 3H, Me), 3.70 (s, 3H, NMe), 3.82 (s, 1H, CH) , 4.78 (br s, 2H, NH$_2$); the minor isomer shows resonances at δ 2.26 (s, 3H, Me), 2.30 (s, 3H, Me), 4.38 (s, CH), 4.42 (br s, 1H NH); ^{13}C-NMR (CDCl$_3$): the major isomer shows resonances at δ 10.52 (q, J=127.1 Hz, Me), 12.70 (q, J=128.1 Hz, Me), 36.05 (q, J=142.2 Hz, NMe), 64.31 (d, J=175 Hz, CH), 114.06 (s, C-4), 119.63 (s, CN), 138.59 (s, C-5), 145.33 (s, C-3), 155.94 (s, C-NH$_2$). Minor isomer shows resonances at δ 10.76 (q), 12.49 (q), 67.21 (d), 112.40 (s), 120.32 (s), 139.25 (s), 145,20 (s), 156.23 (s). *Anal.* Calcd for C$_9$H$_{12}$N$_4$: C, 61.34; H, 6.86; N, 31.79. Found: C, 61.30; H, 6.89; N, 31.75.

The same compound (**2b**) was obtained according to the *method B* in 74% yield.

Reactions of 1a with ethylhydrazine

Following the *method A*, 3-amino-3-(3,5-dimethyl-1-ethylpyrazol-4-yl)propenenitrile (**2c**) was obtained as pale yellow crystals, yield 75% (purified by flash column chromatography, eluent ethyl acetate: light petroleum 8:2), mp 146-148°C (triturated with light petroleum); IR (KBr): 3392, 3218, 2182, 1650, 1581 cm^{-1}; ^{1}H-NMR (CDCl$_3$): δ 1.38 (t, J=7.2 Hz, 3H, Me), 2.27 (s, 3H, Me), 2.31 (s, 3H, Me), 3.84 (s, 1H, CH), 4.03 (q, J=7.2 Hz, 2H, CH$_2$), 4.77 (br s, 2H, NH$_2$). *Anal.* Calcd for C$_{10}$H$_{14}$N$_4$: C, 63.13; H, 7.42; N, 29.45. Found: C, 63.17; H, 7.40; N, 29.47.

The same product (**2c**) was obtained according to *method B* in 18% yield.

Reactions of 1a with phenylhydrazine

When the reaction was carried out according the *method A*, stirring at rt for 3 d, the following compounds were obtained after purification of the reaction mixture by flash column chromatography (eluent ethyl acetate: light petroleum 1:1):

5-Cyanomethylene-3-methyl-1-phenylpyrazole (**4**, R=Ph): Rf 0.72, oil, yield 18%, IR (neat) 2255, 1597, 1553, 1503 cm^{-1}; ^{1}H-NMR (CDCl$_3$): δ: 2.33 (s, 3H, Me), 3.71 (s, 2H, CH$_2$), 6.35 (s, 1H, CH), 7.30-7.60 (5H, Ph); ^{13}C-NMR (CDCl$_3$): δ 13.55 (q, J=126.8 Hz, Me), 16.06 (t, J=135.3 Hz, CH$_2$), 107.88 (d, J=174.2 Hz, C-4), 115.83 (s, CN), 125.19 (d, J=166.6 Hz, Ph), 128.69 (d, J=168.5 Hz, Ph), 129.65 (d, J=161.0 Hz, Ph) 131.91 (dt, J=4.7 and 7.0 Hz, C-5), 138.35 (s, Ph), 149.77 (dq, J=7.8 Hz, C-3). *Anal.* Calcd for C$_{12}$H$_{11}$N$_3$: C, 73.07; H, 5.62; N, 21.30. Found: C, 73.01; H, 5.68; N, 21.25.

3-Amino-5-oxo-3-hexenenitrile (**3**): Rf 0.36, colourless crystals, mp 103-106°C (ethyl acetate/light petroleum) (lit.,[7] mp 108-112°C), yield 24%; IR (KBr) 3361, 2193, 1633, 1530 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ 2.10 (s, 3H, Me), 3.32 (s, 2H, CH$_2$), 5.24 (s, 1H, CH), 5.50 (br, 1H, NH), 9.63 (br, 1H, NH).

N-Acetylphenylhydrazine: Rf 0.20, colourless crystals, mp 125-127 °C (triturated with light petroleum) (lit.,[8] mp 128-131°C), yield 40%.

When the reaction was carried out according to the *method B* 3-amino-3-(3,5-dimethyl-1-phenylpyrazol-4-yl)propenenitrile (**2d**) was obtained as pale yellow crystals, yield 63% (purified by flash column chromatography, eluent ethyl acetate: light petroleum 8:2): mp 117-120°C (ethyl acetate/light petroleum);

IR (KBr): 3334, 3200, 2183, 1636, 1593, 1504 cm⁻¹; ¹H-NMR (CDCl₃): two geometric isomers are present in 4:1 molar ratio. Major isomer shows absorptions at δ 2.33 (s, 3H, Me), 2.34 (s, 3H, Me), 3.93 (s, 1H, CH), 4.89 (br s, 2H, NH₂), 7.35-7.48 (m, 5H, Ph); minor isomer shows absorptions at δ 2.46 (s, 3H, Me), 2.49 (s, 3H, Me), 4.45 (s, 1H, CH), 4.64 (br s, 2H, NH₂). *Anal.* Calcd for C₁₄H₁₄N₄: C, 70.57; H, 5.92; N, 23.51. Found: C, 70.50; H, 5.88; N, 23.48.

Reactions of 1a with p-nitrophenylhydrazine

When the reaction was carried out according to the *method A*, stirring at rt for 3 days, 3-amino-5-*p*-nitrophenylhydrazino-3-hexenenitrile (**5**) was obtained in 33 % yield (purified by flash column chromatography, eluent ethyl acetate: light petroleum 1:1), mp 115-117°C (triturated with light petroleum); IR (KBr) 3418, 3343, 2185, 1657, 1600, 1307 cm⁻¹; ¹H-NMR (DMSO-d₆): δ 1.93 (s, 3H, Me), 3.06 (s, 2H, CH₂), 3.69 (s, 1H, CH), 6.59 (s, 2H, exchanges with D₂O, NH₂), 7.19 (d, J=9.2 Hz, 2H, Ph), 8.08 (d, J=9.2 Hz, 2H, Ph), 9.90 (s, 1H, exchanges with D₂O, NH); ¹³C-NMR (DMSO-d₆): δ 15.39 (q, J=127.0 Hz, Me), 43.87 (t, J= 145.0 Hz, CH₂), 58.87 (d, J=175.3 Hz, CH), 111.48 (d, J= 164.5 Hz, Ph), 119.96 (s, CN), 125.76 (d, J=169.5 Hz, Ph), 138.03 (s, Ph), 147.49 (s, Ph), 151.43 (s, C-5), 161.67 (s, C-3). *Anal.* Calcd for C₁₂H₁₃N₅O₂: C, 55.59; H, 5.05; N, 27.01. Found: C, 55.52; H, 5.08; N, 26.91.

The same reaction carried out according to the *method B* afforded 3-amino-3-(3,5-dimethyl-1-*p*-nitrophenylpyrazol-4-yl)propenenitrile (**2e**) as pale yellow crystals, yield 48%, mp 228-230°C (triturated with ethyl acetate); IR (KBr): 3433, 3343, 2195, 1643, 1593, 1518, 1351 cm⁻¹; ¹H-NMR (DMSO-d₆): δ 2.28 (s, 3H, Me), 2.44 (s, 3H, Me), 4.36 (s, 1H, CH), 6.80 (br, 2H, NH₂), 7.63-8.40 (A₂B₂, J=8.9 Hz, 4H, Ph); ¹³C-NMR (DMSO-d₆): δ 12.23 (q, J=129.1 Hz, Me), 12.41 (q, J=127.1 Hz, Me), 63.12 (d, J=166.7 Hz, CH), 117.58 (s, CN), 121.91 (s, C-4), 123.95 (d, J=167.2 Hz, Ph), 124.97 (d, J=169.0 Hz, Ph), 139.00 (s, C-5), 143.98 (s, Ph), 145.51 (s, Ph), 148.46 (s, C-3), 156.74 (C-NH₂). *Anal.* Calcd for C₁₄H₁₃N₅O₂: C, 59.36; H, 4.63; N, 24.72. Found: C, 59.34; H, 4.66; N, 24.68.

Reaction of 1b with hydrazines

General procedure

To a solution of **1b** (0.33 g, 2 mmol) in acetic acid (10 mL) the pertinent hydrazine (2.2 mmol) was added. The reaction mixture was stirred at rt for 3 d, concentrated under reduced pressure to give a residue which was purified by flash column chromatography.

Reactions of 1b with hydrazine hydrate

After purification by flash chromatography (eluent ethyl acetate: methanol 9.5:0.5) 1,4-diamino-6-methyl-5-methoxycarbonylpyridin-2-one (**7a**) was obtained as colourless crystals, yield 41%, mp 191-194°C (triturated with light petroleum); IR (KBr) 3468, 3342, 3295, 1681, 1632, 1594 cm⁻¹; ¹H-NMR (DMSO-d₆): δ 2.50 (s, 3H, Me), 3.78 (s, 3H, OMe), 5.46 (s, 1H, CH), 5.83 (s, 2H, NH₂), 6.31 (s, 2H, NH₂); ¹³C-NMR (DMSO-d₆): δ: 17.97 (q, J=129.8 Hz, Me), 51.87 (q, J=146.5 Hz, OMe), 90.04 (d, J=162.1 Hz, CH), 99.33 (s, C-5), 150.58 (s, C-6), 153.79 (s, C-2 or C-4), 159.51 (s, C-4 or C-2), 166.98 (s, COO). *Anal.* Calcd for C₈H₁₁N₃O₃: C, 48.73; H, 5.62; N, 21.31. Found: C, 48.66; H, 5.68; N, 21.25.

Reaction of 1b with methylhydrazine

After purification by flash chromatography (eluent ethyl acetate: methanol 9.5:0.5) 4-amino-6-methyl-

1-methylamino-5-methoxycarbonylpyridin-2-one (**7b**) was obtained as colourless crystals, yield 41%, mp 154-156°C (triturated with light petroleum); IR (KBr) 3430, 3283, 3210, 1706, 1636 cm^{-1}; ^{1}H-NMR (DMSO-d_6): δ 2.63 (d, J=4.8 Hz, 3H, Me), 2.71 (s, 3H, Me), 3.87 (s, 3H, OMe), 5.61 (s, 1H, CH), 5.67 (br s, 2H, NH$_2$), 6.16 (q, J=4.8 Hz, 1H, NH). *Anal.* Calcd for C$_9$H$_{13}$N$_3$O$_3$: C, 51.18; H, 6.20; N, 19.89. Found: C, 51.12; H, 6.24; N, 19.92.

Reaction of 1b with phenylhydrazine

After purification by flash chromatography (eluent: methylene chloride: methanol: toluene: 17:2:1) two compounds were obtained:

5-Cyanomethylene-3-methyl-4-methoxycarbonyl-1-phenylpyrazole (**8**), colourless crystals, mp 70-74°C (ethyl acetate/light petroleum), yield 28%; IR (KBr): 2258, 1715, 1556, 1556, 1506 cm^{-1}; ^{1}H-NMR (CDCl$_3$): δ 2.51 (s, 3H, Me), 3.92 (s, 3H, OMe), 7.40-7.60 (m, 5H, Ph); ^{13}C-NMR (CDCl$_3$): δ 13.97 (q, J= 128.5 Hz, Me), 15.56 (t, J=146.6 Hz, CH$_2$), 51.44 (q, J= 146.4 Hz, OMe), 111.71(s, C-4), 114.99 (s, CN), 125.49 (d, J= 162.5 Hz, Ph), 129.53 (d, J=163.1 Hz, Ph), 129.70 (d, J=163.1 Hz, Ph), 135.85 (t, ^{2}J=7.4 Hz, C-5), 137.33 (s, Ph), 151.78 (q, ^{2}J=6.7 Hz, C-3), 163.65 (s, COO). *Anal.* Calcd for C$_{14}$H$_{13}$N$_3$O$_2$: C, 65.87; H, 5.13; N, 16.46. Found: C, 65.80; H, 5.16; N, 16.42

4-Amino-2-imino-5-methoxycarbonyl-6-methyl-1-phenylamino-1,2-dihydro-pyridine acetate (**6**) was obtained as oil, yield 24%, IR (KBr): 3356 br, 1704, 1633, 1495 cm^{-1}; ^{1}H-NMR (CDCl$_3$): δ 2.07 (s, Me), 2.62 (s, Me), 3.89 (s, OMe), 5.75 (s, 1H, CH), 5.82 (br s, 1H, NH), 6.62 (d, J=7.9 Hz, 2H, Ph), 6.94 (t, J=7.5 Hz, 1H, Ph), 7.16-7.26 (m, 2H, Ph), 8.00 (br s, 1H, NH), 8.00-9.00 (br, 2H, NH$_2$); ^{13}C-NMR (CDCl$_3$): δ 18.24 (q, J=132.0 Hz, Me), 20.94 (q, J=128.4 Hz, Me), 52.21 (q, J=150.2 Hz, OMe), 93.54 (d, J=163.6 Hz, CH) , 101.62 (s, C-5), 113.61 (d, J=156.6 Hz, Ph) , 122.16 (d, J= 161.8 Hz, Ph), 129.41 (d, J=158.0 Hz, Ph), 146.41 (s, Ph), 155.55 (s, C-4 or C-6), 155.84 (s, C-6 or C-4), 162.00 (s, COO), 167.43 (s, COO), 176.37 (s, C-2). *Anal.* Calcd for C$_{16}$H$_{20}$N$_4$O$_4$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.75; H, 6.02; N, 16.82.

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