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5-Aminopyrazoles from Enolisable Ketones and 1-Cyano-1-Alkylhydrazines.

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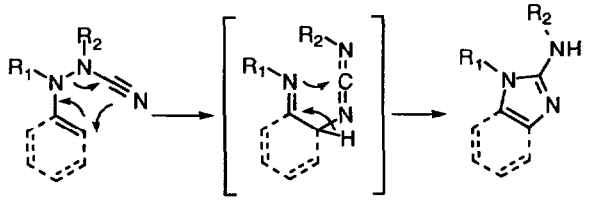
In memory of Dr Zdenek Janousek, deceased on July 17th 1996.

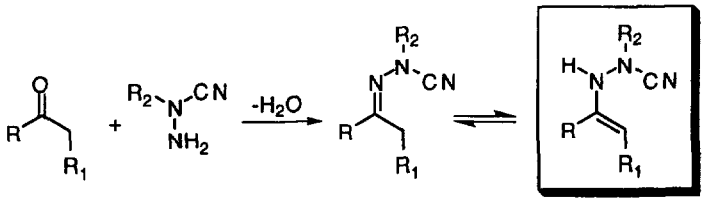
Abstract: The reaction of enolisable ketones with 1-alkyl-1-cyanohydrazines leads to the corresponding cyanohydrazones. These compounds cyclise under thermal or mildly basic conditions, furnishing the corresponding 5-aminopyrazoles in good yield. In some cases, the hydrazones cannot be isolated, and the pyrazole derivatives are directly obtained. Hydrazone-enehydrazine tautomerism was observed, but no subsequent [3,3] rearrangement.

The [3,3] rearrangement of aryl- and vinyl- cyanohydrazines provides after *in situ* cyclisation an interesting access to 2-aminobenzimidazoles and 2-aminoimidazoles[1-3]. Yields are essentially quantitative and, in some cases, the reaction takes place even at room temperature (Scheme 1).



Scheme 1

As part of our study of this rearrangement, cyanohydrazones were examined as potential precursors of the corresponding 1-cyano 2-vinyl hydrazines, through hydrazone-enehydrazine tautomerism (Scheme 2).



Scheme 2

[1]Fax : 32-10-47 27 88

However, when 1-cyano-1-methylhydrazine was allowed to react with 2,4-pentanedione without solvent for two days at 60°C, only the 1-methyl-4-acetyl-5-aminopyrazole **2a** could be obtained in 78% yield. The structure of **2a** has been confirmed by single-crystal X-ray analysis (Figure 1).

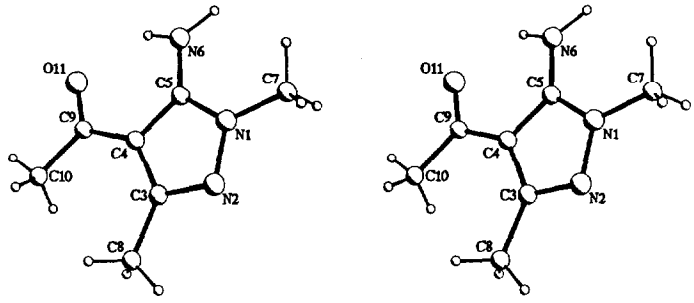
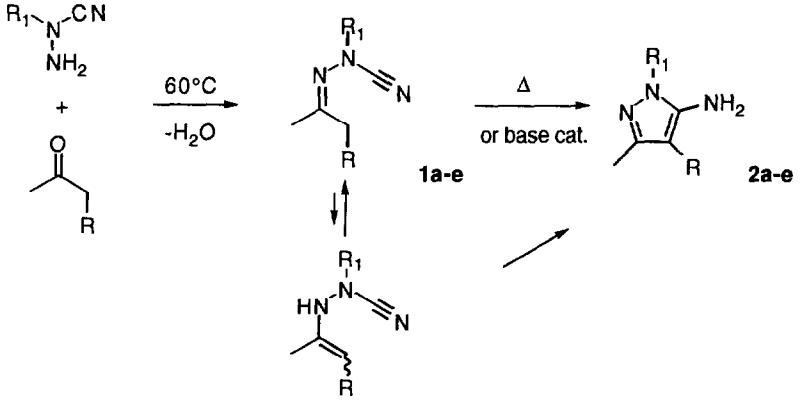


Figure 1: Stereoscopic view of **2a**[4].

The reaction also proceeds well in apolar solvents such as toluene. With less enolised carbonyl compounds, the corresponding hydrazones (**1d-e**) were isolated in good yield. Interestingly, even though ^{1}H NMR shows that the ethyl acetoacetate hydrazone **1d** is in a 5:1 equilibrium with the corresponding ene-hydrazine, the [3,3] rearrangement could not be observed (Scheme 3, Table 1).



Scheme 3

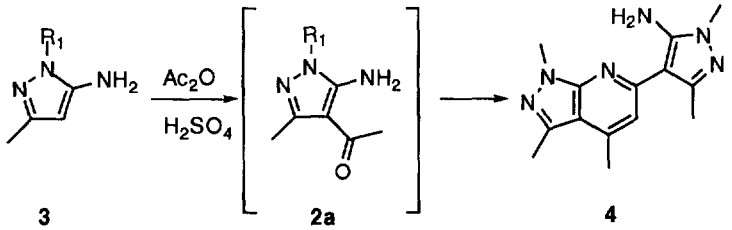
Table 1

Entry	R	R_1	Yield of **1**	Yield of **2**
a	$COCH_3$	CH_3	not isolated	78
b	$COCF_3$	CH_3	not isolated	75
c	$COCH_3$	$PhCH_2$	not isolated	73
d	COOEt	CH_3	87	90
e	Ph	CH_3	71	66

In the case of the trifluoro derivative **2b**, only one regioisomer was obtained. When the hydrazones could be isolated, treatment with a catalytic amount of base in THF or ethanol yielded the corresponding pyrazole in two hours at room temperature. Thus, hydrazone **1e**, obtained from 1-cyano-1-methylhydrazine and benzyl methyl ketone, gave the corresponding pyrazole in 66% yield by treatment with 0.05 equivalent of potassium t-butoxyde in dry THF. Treatment of hydrazone **1d** with a trace amount of KOH in ethanol allowed the recovery of the pyrazole **2d** in 90% yield. Refluxing the same hydrazone in toluene for 3 days gave **2d** in 75% yield.

5-Aminopyrazoles are usually prepared[5] through the condensation of alkylhydrazines with β-substituted acrylonitriles[6,7]; however the pyrazoles **2a-c** are new, as well as the hydrazones **1d-e**.

Ambiphilic pyrazoles such as **2a-e** could be useful for the preparation[7-9] of fused pyrazoles such as Allopurinol, an inhibitor of xanthine oxidase used for the treatment of gout. Furthermore, the easy replacement of the amino moiety by a chlorine atom has allowed the preparation[10,11] of other fused heterocycles. Pyrazole **2a** had been postulated[12] as an intermediate during the acetylation of 1-methyl 5-aminopyrazole **3**, but had not been isolated. Under the acetylation conditions it dimerised, to give the pyrazolopyrimidine **4** (Scheme 4).



Scheme 4

Under our reaction conditions, the cyclisation was not observed and **2a** could be prepared in good yield. Thus, this method allows an easy access to 1-alkyl-5-aminopyrazoles bearing a 4-substituent, from readily available 1-alkyl-1-cyanohydrazines and various ketones, under mild conditions.

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EXPERIMENTAL

General

TLC was carried out on silica gel plates (Merck 60F254) and visualised under U.V. light. Flash chromatography was carried out with silica gel (Merck 60; 230-400 Mesh). Melting points were determined on a Buchi (Dr. Tottoli) apparatus, and are uncorrected. ^{1}H NMR were recorded in $CDCl_3$ solution, using TMS as internal reference at 200MHz on a Varian Gemini or XL 200 spectrometer. Mass spectra (EI, 70 eV) were recorded on a Varian AMT 44S spectrometer.

Synthesis of **1-cyano-1-methyl hydrazine**. To a precooled (0°C) solution of 4.50 gr (42.5 mmoles, 1 equivalent) of cyanogen bromide (CAUTION) in 100 ml of dichloromethane, a mixture of 2.00 gr (42.5 mmoles, 1 equivalent) of methyl hydrazine (CAUTION), 2.50 gr (21.3 mmoles, 0.5 equivalent) of sodium carbonate and 20 ml of water is added dropwise under vigorous stirring. When the evolution of gas stops, the two layers are separated, the aqueous phase is extracted three times with methylene chloride, the organic phases are joined and dried over magnesium sulfate. The solvent is removed under reduced pressure, affording 2.11 gr of an oil (70%), which was used without further purification. Attempted distillation only led to extensive decomposition, while chromatography on silica gel did not improve the elemental analysis. **^{1}H NMR** ($CDCl_3$) δ: 3.1 (s, CH_3), 4.3 (m, NH_2). **^{13}C NMR** ($CDCl_3$) δ: 44.4 (Q, 141, NCH_3), 117.7 (S, CN). **MS**: 71 ($[M]^{\cdot+}$), 56. **IR** (film, cm^{-1}): 2214 (CN st), 2940, 3200, 3337.

Synthesis of **1-benzyl-1-cyano hydrazine**. In a three necked flask, a solution of 13.00 gr (122.75 mmoles, 1 equivalent) of cyanogen bromide (CAUTION) in 200 ml of dichloromethane is cooled to 0°C. Two addition funnels are fitted to the flask, one containing 15.00 gr (122.75 mmoles, 1 equivalent) of benzylhydrazine (CAUTION) dissolved in 50 ml of methylene chloride, the second containing a solution of 6.50 gr (61.4 mmoles, 0.5 equivalent) of sodium carbonate in 50 ml of water. While maintaining the temperature at 0°C, the content of the two funnels is added simultaneously under vigorous stirring. When the evolution of gas stops, the two layers are separated, the aqueous phase is extracted three times with methylene chloride, the organic phases are joined and dried over magnesium sulfate. The solvent is removed under reduced pressure, and the resulting yellow oil is purified by chromatography (Ethyl Acetate/Petroleum Ether 1/1), affording 13.55 gr (75%) of colourless cristals (m.p. 43°C). **^{1}H NMR** ($CDCl_3$) δ: 4.0 (m, NH_2), 4.3 (s, CH_2), 7.0-7.5 (m, arom CH). **^{13}C NMR** ($CDCl_3$) δ: 60.4 (T, 141, NCH_2), 117.7 (S, CN), 126.0 (D, 160, arom CH), 128.6 (D, 160, arom CH), 128.7 (D, 160, arom CH), 133.2 (S, arom C). **MS**: 121 ($[M\text{-}CN]^{\cdot+}$), 91, 56. **IR** (KBr, cm^{-1}): 1496, 1609, 2215 (CN st). Anal. Calcd. for $C_8H_9N_3$: C 65.29%, H 6.16%, N 28.55%; found C 65.41%, H 6.05%, N 28.80%.

General procedure for the synthesis of pyrazoles **2a-c** and hydrazones **1d-e**. In a 10 ml flask, 1 equivalent of the ketone and 1 equivalent of the 1-alkyl-1-cyano hydrazine (CAUTION) are mixed. The mixture is heated at 60°C with stirring for 12 or 48 hours. The resulting mixture is dissolved in methylene chloride, the water is removed by decantation and the solution is dried over magnesium sulfate. After removing the solvent under reduced pressure, the residue is purified by chromatography on silica gel.

Synthesis of **1,3-dimethyl-4-acetyl-5-aminopyrazole 2a**. From 1.36 gr (13.6 mmoles, 1 equivalent) of 2,4-pentanedione and 1.00 gr (13.6 mmoles, 1 equivalent) of 1-cyano-1-methylhydrazine. Purified by chromatography (Ethyl Acetate/Petroleum Ether 1/1), affording 1.64 gr (78%) of a white powder (m.p. 143-144°C). **^{1}H NMR** ($CDCl_3$) δ: 2.60 (s, CH_3), 2.61 (s, CH_3), 3.77 (s, NCH_3), 6.39 (m, NH_2). **^{13}C NMR** ($CDCl_3$) δ: 15.4 (Q, 128, CH_3), 29.0 (Q, 127, $COCH_3$), 32.9 (Q, 140, NCH_3), 104.6 (S, C-$COCH_3$), 147.0 (Sq, 7, C-CH_3), 150.8 (Sq, 2 (^{3}J), C-NH_2), 192.6 (Sq, 6, CO). **MS**: 153 ($[M]^{\cdot+}$), 138 ($[M\text{-}CH_3]^{\cdot+}$). **IR** (KBr, cm^{-1}): 1611 (C=N str.), 3250, 3281 (N-H str.). Anal. Calcd. for $C_7H_{11}N_3O$: C 54.88%, H 7.24%, N 27.43%; found C 55.05%, H 7.27%, N 27.65%.

The crystallographic data are as follows: $C_7H_{11}N_3O$, M_r = 153.19, orthorhombic, *Pbca*, a = 10.058 (1), b = 10.168 (1), c = 15.756 (1) Å, V = 1611.4 (2) Å^3, Z = 8, D_x = 1.26 g cm^{-3}, μ = 7.3 cm^{-1}, F (000) = 656, T = 291K. Crystals were obtained by recrystallisation in ethyl acetate. Parallelepiped crystals with dimensions 0.20 x 0.20 x 0.15mm. Lattice parameters refined using 20 reflections in the range $20° \leq 2\theta \leq 60°$. Huber four circle diffractometer with Rigaku rotating anode generator, graphite monochromatized Cu$K\alpha$ radiation (λ = 1.54178Å). 1455 independent reflections with $\sin\theta/\lambda \leq 0.60$Å^{-1}; $0 \leq h \leq 12$, $0 \leq k \leq 12$, $0 \leq l \leq 18$, 1293 with $I \geq 2.5\sigma(I)$. A standard reflection (1 2 5) was checked every 50 reflections, no significant deviation was observed. Structure solved by direct methods using SHELXS86[13]. All H atoms from difference Fourier synthesis. Anisotropic least squares refinement (SHELX76)[14] using F; H isotropic with common refined temperature factor (U = 0.09 Å^2). 134 parameters. $w = 1/(\sigma^2 + 0.00008F^2)$, R = 0.067, wR = 0.054, S = 4.76 for 1293 observed reflections. Final maximum shift to error = 0.04. Maximum and minimum heights in final difference Fourier synthesis = 0.31 and -0.65 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol.IV).

Synthesis of **1,3-dimethyl-4-trifluoroacetyl-5-aminopyrazole 2b**. From 1.08 gr (7.0 mmoles) of 1,1,1-trifluoro-2,4-pentanedione and 0.50 gr (7.0 mmoles) of 1-cyano-1-methylhydrazine. Purified by

chromatography (Ethyl Acetate), affording 1.09 gr (75%) of a white powder (m.p. 119°C). **^{1}H NMR** ($CDCl_3$) δ: 2.3 (s, CH_3), 3.6 (s, NCH_3), 6.2 (m, NH_2) **^{13}C NMR** ($CDCl_3$) δ: 14.5 (Qq, 120, 7 ($^5J_{C-F}$), CH_3), 33.2 (Q, 140, NCH_3), 99.8 (S, C-$COCF_3$), 116.7 (Q, 290, CF_3), 147.2 (Sq, 7 ($^4J_{C-F}$), C-CH_3), 153.9 (S, C-NH_2), 173.5 (Sq,37 ($^2J_{C-F}$), CO). **M.S.** 207 ($[M]^{\cdot+}$), 138 ($[M-CF_3]^{\cdot+}$). **I.R.** (KBr, cm^{-1}): 1564, 1617, 1649 (C=N str.), 3216, 3230 (N-H str.). Anal. Calcd. for $C_7H_8F_3N_3O$: C 40.58%, H 3.89%, N 20.28%; found C 40.84%, H 3.66%, N 20.25%.

Synthesis of **1-benzyl-3-methyl-4-acetyl-5-aminopyrazole 2c**. From 1.36 gr (13.6 mmoles, 1 equivalent) of 2,4-pentanedione and 2.00 gr (13.6 mmoles, 1 equivalent) of 1-benzyl-1-cyanohydrazine. Purified by chromatography (Ethyl Acetate/Petroleum Ether 1/1), affording 2.28 gr (73%) of a white powder (m.p. 114°C). **^{1}H NMR** ($CDCl_3$) δ: 2.28 (s, CH_3), 2.31 (s, CH_3), 4.95 (s, CH_2), 6.15 (m, NH_2), 7.0-7.4 (s, arom CH). **^{13}C NMR** ($CDCl_3$) δ: 15.4 (Q, 128, CH_3), 28.6 (Q, 127, $COCH_3$), 49.7 (T, 135, $PhCH_2$), 104.5 (S, C-$COCH_3$), 126.3 (Dm, 158, arom CH), 127.3 (Ddd, 162, arom CH), 128.3 (Dd, 161, arom CH), 135.1 (S, Ph), 147.4 (S, C-CH_3), 150.8 (S, C-NH_2), 192.6 (S, CO) **MS**: 229 ($[M]^{\cdot+}$), 214 ($[M-CH_3]^{\cdot+}$), 91 ($[PhCH_2]^{\cdot+}$). **IR** (KBr, cm^{-1}): 831, 1595, 1669 (CO str.). Anal. Calcd. for $C_{13}H_{15}N_3O$: C 70.00% H 6.27% N 17.41%; found C 69.85% H 6.29% N 16.98%.

Synthesis of the **N-cyano-N-methylhydrazone of ethyl acetoacetate 1d**. From 3.42 gr (26.3 mmoles) of ethyl acetoacetate and 2.00 gr (26.3 mmoles) of 1-cyano-1-methylhydrazine (CAUTION). Purified by chromatography (Ethyl Acetate/Petroleum Ether 1/3), affording 4.50 gr (87%) of a colorless oil. The product is a 5 to 1 mixture of the title hydrazone and the corresponding enehydrazine. Hydrazone tautomer (major): **^{1}H NMR** ($CDCl_3$) δ: 1.3 (t, 7, OCH_2CH_3), 2.2 (s, CH_3), 3.24 (s, NCH_3), 3.33 (s, CH_2), 4.19 (q, 7, OCH_2CH_3). **^{13}C NMR** ($CDCl_3$) δ: 13.5 (Q, OCH_2CH_3), 17.4 (Q, CH_3), 42.5 (Q, NCH_3), 43.6 (T, CH_2), 60.6 (T, OCH_2CH_3), 113.6 (S, CN), 163.2 (S, C=N), 168.0 (S, CO). Enehydrazine tautomer (minor): **^{1}H NMR** ($CDCl_3$) δ: 1.3 (t, 7, OCH_2CH_3), 2.14 (s, CH_3), 3.17 (s, NCH_3), 3.5 (s, CH), 4.2 (q, 7, OCH_2CH_3), 4.5 (s, NH), **^{13}C NMR** ($CDCl_3$) δ: 13.9 (Q, OCH_2CH_3), 23.1 (Q, CH_3), 42.3 (Q, NCH_3), 61.0 (T, OCH_2CH_3), 88.9 (D, CH), 114.5 (S, CN), 165.5 (S, C-N), 166.7 (S, CO). **MS**: 183 ($[M]^{\cdot+}$), 137 ($[M-EtOH]^{\cdot+}$), 109 ($[M-EtOH-CO]^{\cdot+}$). Anal. Calcd. for $C_8H_{13}N_3O_2$: C 52.44% H 7.151% N 22.93%; found C 52.28% H 6.96% N 22.59%.

Synthesis of the **N-cyano-N-methylhydrazone of benzyl methylketone 1e**. From 3.77 gr (28.2 mmoles) of ethyl acetoacetate and 2.00 gr (28.2 mmoles) of 1-cyano-1-methylhydrazine (CAUTION). Purified by chromatography (Ethyl Acetate/Petroleum Ether 1/10), affording 5.21 gr (71%) of a colorless oil. Alternatively, the product can also be purified by distillation (195°C/ 0.09 mmHg). The product is a 5 to 1 mixture of the E and Z hydrazones. E isomer (major): **^{1}H NMR** ($CDCl_3$) δ: 2.0 (s, CH_3), 3.23 (s, NCH_3), 3.57 (s, CH_2), 7-7.5 (m, Ph). **^{13}C NMR** ($CDCl_3$) δ: 17.2 (Q, 126, CH_3), 43.0 (Q, 141, NCH_3), 45.0 (T, 130, CH_2), 114.8 (S, CN), 127.1 (Dt , 160, 7, arom CH), 128.7 (D, 160, arom CH), 128.9 (D, 161, arom CH), 135.6 (S, arom C), 169.2 (S, C=N). Z isomer (minor): **^{1}H NMR** ($CDCl_3$) δ: 1.9 (s, CH_3), 3.2 (s, NCH_3), 3.8 (s, CH_2), 7-7.5 (m, Ph). **^{13}C NMR** ($CDCl_3$) δ: 22.8 (Q, 126, CH_3), 38.4 (T, 130, CH_2), 52.0 (Q, 141, NCH_3), 114.8 (S, CN), 127.1 (Dt, 160, 7, arom CH), 128.7 (D, 160, arom CH), 128.9 (D, 161, arom CH), 135.6 (S, arom C), 169.6 (S, C=N). **MS**: 187 ($[M]^{\cdot+}$), 96 ($[M-PhCH_2]^{\cdot+}$), 91 ($[PhCH_2]^{\cdot+}$), 69, 55 ($[MeNCN]^{\cdot+}$). **IR** (film, cm^{-1}): 1632 (C=N str.), 2204 (CN str). Anal. Calcd. for $C_{11}H_{13}N_3$: C 70.56% H 7.00% N 22.44% ; found C 70.32% H 7.13% N 22.60%.

Synthesis of the **1,3-dimethyl-4-ethoxycarbonyl-5-aminopyrazole 2d**. 1.10 gr of the hydrazone **1d** are dissolved in 50 ml of ethanol containing 0.10 gr of KOH. The reaction mixture is stirred at room temperature for two hours. The solvent is then evaporated under reduced pressure, the residue is partitioned between 50ml of methylene chloride and 20 ml of water. The organic phase is separated and dried over magnesium sulfate. The solvent is evaporated under reduced pressure, and the resulting solid is purified by chromatography (Ethyl Acetate), affording 1.00 gr (90%) of a white powder (m.p. 111°C, litt 111-113°C[15-17]). **^{1}H NMR** ($CDCl_3$) δ: 1.3 (t, 7, OCH_2CH_3), 2.3 (s, CH_3), 3.5 (s, NCH_3), 4.3 (q, 7, OCH_2CH_3), 5.2 (m, NH_2). **^{13}C NMR** ($CDCl_3$) δ: 14.25 (Q, 122, CH_3), 14.34 (Q, 122, OCH_2CH_3), 33.4 (Q, 139, NCH_3), 59.1 (T, 147, OCH_2CH_3, 94.2 (S, C-CO_2Et), 148.7 (Sq, 2, C-CH_3) , 150.2 (S, C-NH_2), 165.0 (S, CO_2Et).

MS: 183 ([M]$^{\cdot+}$), 137 ([M-EtOH]$^{\cdot+}$). Anal. Calcd. for $C_8H_{13}N_3O_2$: C 52.45% H 7.15% N 22.94%; found C 52.69% H 7.10% N 23.08%.

Synthesis of the **1,3-dimethyl-4-phenyl-5-aminopyrazole 2e**[18]. 1.00 gr (5.3 mmoles, 1 equivalent) of the hydrazone **1e** is dissolved in 50 ml of dry THF containing 0.03 gr (0.3 mmole, 0.06 equivalent) of potassium t-butoxide. After stirring the reaction mixture at room temperature for two hours, the solvent is evaporated under reduced pressure, and the residue is partitioned between 50ml of ethyl acetate and 10 ml of water. The organic phase is separated and dried over magnesium sulfate. The solvent is evaporated under reduced pressure, and the resulting solid is purified by chromatography (Ethyl Acetate), affording 0.66 gr (66%) of a yellow solid (m.p. 139°C). **^{1}H NMR** ($CDCl_3$) δ: 2.2 (s, CH_3), 3.6 (s, NCH_3), 3.7 (m, NH_2), 7.0-7.4 (m, Ph).**^{13}C NMR** ($CDCl_3$) δ: 12.8 (Q, 127, $\underline{C}H_3$), 34.0 (Q, 139, $N\underline{C}H_3$), 104.9 (Sm, C-Ph), 125.7 (Ddd, 160, 7, 7, arom CH), 128.3 (Ddd, 162, 7, 7, arom CH), 128.7 (Dd, 160, 7, arom CH), 133.7 (Sdd, arom C), 142.0 (S, $\underline{C}$-NH_2), 144.7 (Sq, 6, $\underline{C}$-CH_3). **MS**: 188 ([MH]$^{\cdot+}$), 187 ([M]$^{\cdot+}$),145, 115. **IR** (KBr, cm^{-1}): 1551, 1603, 1639. Anal. Calcd. for $C_{11}H_{13}N_3$: C 70.56% H 6.997% N 22.44%; found C 70.47% H 7.02% N 22.38%.

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