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Cyanoacetaldehyde – New Synthetic Applications of an Old Compound
Syntheses with Nitriles, XCI [1]

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Summary. Various reactions of cyanoacetaldehyde (**1**), freshly prepared by ozonization of (*E*)-1,4-dicyano-2-butene or allylcyanide, are described. Thus, conversion of **1** with anilines gave *β*-phenylaminoacrylonitriles **2a–e**. Reaction of **1** with hydrazines led to the corresponding hydrazones **3a–e**, which could be cyclized under alkaline conditions to 5-aminopyrazoles **4a–d**. An aldol-type condensation product **5a** could be obtained by reaction of **1** with sodiumphenoxide. Treatment of **1** with dimethylformamide-dimethylacetal led to the formation of (*E*)-3-dimethylamino-2-formylpropenenitrile (**6**), a very useful synthon in synthetic chemistry. For the determination of the structure of **6** the method of steady state differential NOEs was used. Reaction of **6** with hydrazines gave 1-substituted-4-cyanopyrazoles **7a–k**.

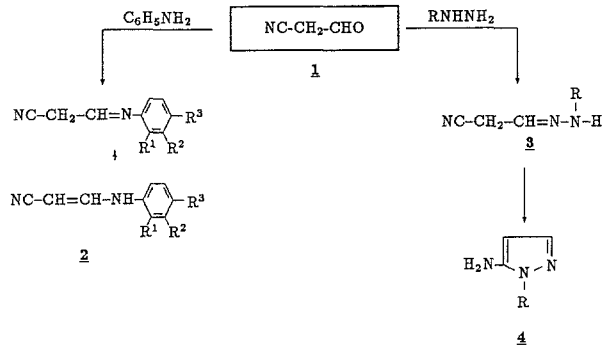
Keywords. Cyanoacetaldehyde; Hydrazones; Cyanopyrazoles; Aminopyrazoles.

Synthesen mit Nitrilen, 91. Mitt. [1]: Cyanoacetaldehyd – Neue synthetische Anwendungen einer bekannten Verbindung

Zusammenfassung. Verschiedene Umsetzungen mit Cyanacetaldehyd (**1**), welcher durch Ozonolyse von (*E*)-1,4-Dicyanbuten oder Allylcyanid hergestellt wurde, werden beschrieben. Reaktion von **1** mit Anilinen führt zu den *β*-Phenylaminoacrylnitrilen **2a–e**. Umsetzungen von **1** mit Hydrazinen ergeben die entsprechenden Hydrazonderivate **3a–e**, welche unter alkalischen Bedingungen zu den 5-Aminopyrazolen **4a–d** cyclisiert werden können. Ein Aldol-ähnliches Kondensationsprodukt **5a** wird durch Reaktion von **1** mit Natriumphenolat erhalten. Erhitzen von **1** in Dimethylformamid-dimethylacetal führt zur Bildung von (*E*)-3-Dimethylamino-2-formylpropennitril (**6**), ein wichtiges Zwischenprodukt für organische Synthesen. Die Struktur kann mit NOE-Experimenten geklärt werden. Reaktion von **6** mit Hydrazinen führt zu 1-substituierten 4-Cyanpyrazolen **7a–k**.

Most recently we have published a new route for the synthesis of cyanoacetaldehyde (**1**) starting from (*E*)-1,4-dicyano-2-butene or allylcyanide by ozonization under reductive conditions to give **1** in 70% yield [2]. Thus, cyanoacetaldehyde and its stable acetal are easily accessible and can be used advantageously for the synthesis especially of various heterocyclic compounds. Sturm and Armbrust [3] reported the in situ synthesis of **1** by reaction of malonoaldehyde-dioxime with nitrous acid and further derivatization of **1**. In contrast to the cited reaction with aniline we

found by ^{1}H-NMR spectroscopy that the obtained products are β-phenylamino-acrylonitriles **2a–e**. Condensation of **1** with hydrazines leads to the hydrazones **3a–d**, which can be cyclized under alkaline conditions to give the 5-aminopyrazoles **4a–d** (Scheme 1).



2	R^1	R^2	R^3
a	H	H	H
b	H	H	CH_3
c	H	Cl	Cl
d	F	H	Cl
e	H	CF_3	H

3	R
a	-C(=O)-OCH3
b	-C(=O)-OC2H5
c	-2,4-dinitrophenyl
d	-C(=O)-C6H4-Cl
e	-C(=O)-C5H4N

4	R
a	-C(=O)-OCH3
b	-C(=O)-OC2H5
c	-2,4-dinitrophenyl
d	-CH2CH2OH

Scheme 1

Treatment of **1** with bases, preferably sodium-phenoxide, gives rise to an aldol type addition and condensation to **5a–b**. Benzoylation of **5b** yields **5c**. With dimethylformamide-dimethylacetal 3-dimethylamino-2-formylpropenenitrile (**6**) is obtained. This offers a new route to an important synthon, known for the synthesis of pyrimidine derivatives [4–6], liquid crystal compositions [7] and thiopyrylium dyes [8]. **6** was first prepared by Trofimenko [9] from 3-amino-2-cyano-acroleine and dimethylamine, but it can also be obtained by Vilsmeier formylation of acetonitrile [10].

For **6** E,Z-isomeric forms can be postulated and by NMR using steady state differential NOE it is possible to distinguish between these isomers. Irradiating the olefinic proton of **6** shows a significant enhancement of the aldehyde proton (20%), the enhancement at the methyl group at 3.27 ppm is much smaller (3%) and vanishes by increasing the temperature according to the enhanced rotation around the C–N bond with a coalescence temperature of 368 K. So **6** exists predominantly in the *E*-form, which is in accordance to ^{1}H-NMR studies with 2-fluoro-3-dimethyl-aminoacroleine [11, 12], and there is an indication that a *s-cis* and a *s-trans* conformation in **6** exists too. By cooling a solution of **6** in $CDCl_3$ to 235 K both conformers can be found in the ^{1}H-NMR spectrum (Fig. 1). The two protons in the *s-cis* conformer are shifted to lower field, the ratio of *s-trans* to *s-cis* is approx. 4:1. A similar effect cannot be observed in *DMSO-d_6* as solvent. It is remarkable

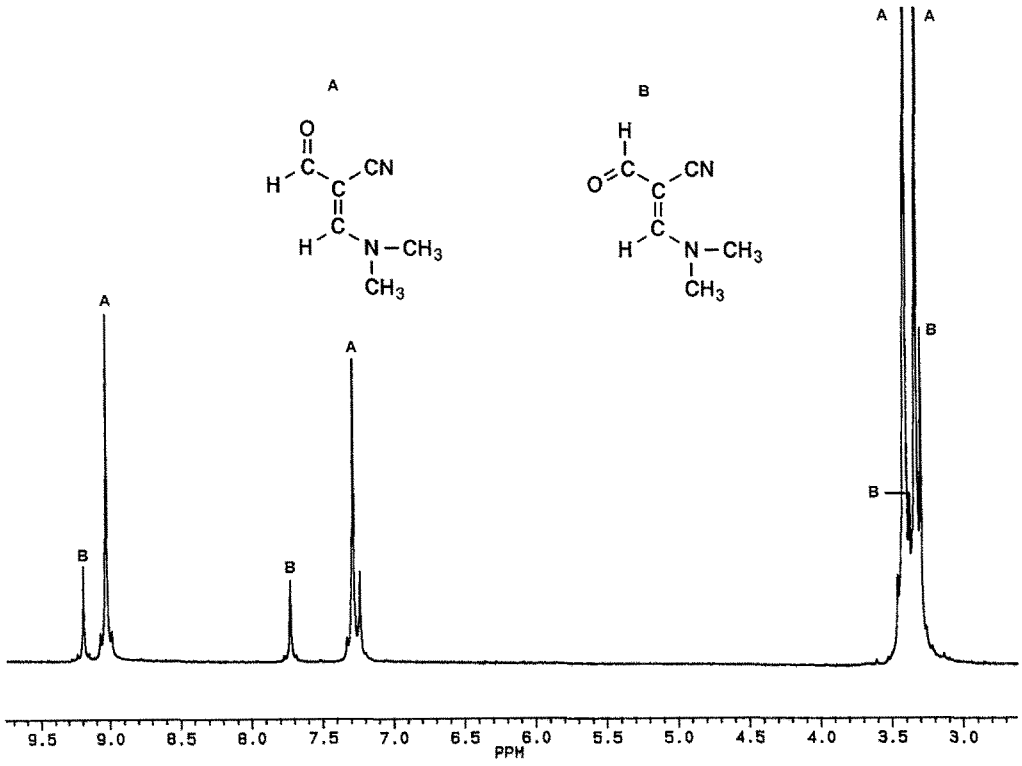
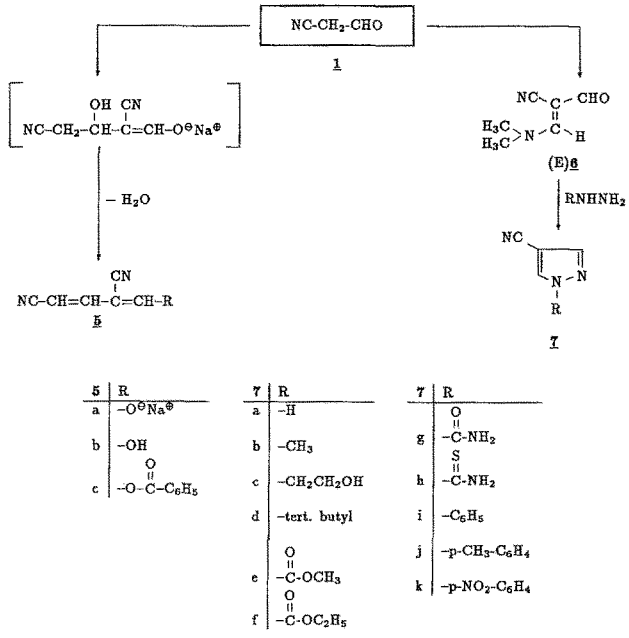


Fig. 1. ^{1}H-NMR spectrum of **6** in $CDCl_3$ at 235 K

that a reaction of **6** with a series of hydrazines under acidic condition occurs by condensation of the hydrazine with the aldehyde function and ring closure by elimination of dimethylamine to give the 4-cyanopyrazoles **7a–k** (Scheme 2).



5	R
a	$-O^{\ominus}Na^{\oplus}$
b	-OH
c	$-O-\overset{O}{\overset{\|}{C}}-C_6H_5$

7	R
a	-H
b	$-CH_3$
c	$-CH_2CH_2OH$
d	-tert. butyl
e	$-\overset{O}{\overset{\|}{C}}-OCH_3$
f	$-\overset{O}{\overset{\|}{C}}-OC_2H_5$

7	R
g	$-\overset{O}{\overset{\|}{C}}-NH_2$
h	$-\overset{S}{\overset{\|}{C}}-NH_2$
i	$-C_6H_5$
j	$-p\text{-}CH_3\text{-}C_6H_4$
k	$-p\text{-}NO_2\text{-}C_6H_4$

Scheme 2

Table 1. Yields, melting points and elemental analysis of acrylonitriles **2a–e**

Compound	Yield (%)	M.p. (°C)	Elemental analysis		C	H	N
2a	30	122–124	$C_9H_8N_2$	calcd.	74.97	5.97	19.43
		(Ref. [14]: 119–121)	(144.2)	found	75.43	5.59	19.31
2b	33	136–138	$C_{10}H_{10}N_2$	calcd.	75.92	6.37	17.71
			(158.2)	found	75.78	6.22	17.65
2c	60	158	$C_9H_6Cl_2N_2$	calcd.	50.37	2.84	13.15
			(213.1)	found	50.63	2.91	12.99
2d	28	128–130	$C_9H_6ClFN_2$	calcd.	54.98	3.08	14.25
			(196.6)	found	55.15	3.08	14.27
2e	20	118	$C_{10}H_7F_3N_2$	calcd.	56.60	3.33	13.20
			(212.2)	found	56.31	3.39	13.15

Table 2. IR and NMR data of β-phenylaminoacrylonitriles **2b–e**

Compound	IR $\nu(cm^{-1})$	^{1}H-NMR ($CDCl_3$) δ(ppm)
2b	3240 (NH), 2200 (CN)	2.22 (s, 3H, CH_3), 4.50 (d, J = 14Hz, 1H, CH=), 6.80–7.43 (m, 4H, aromatic H), 7.76 (dd, J = 12Hz, J = 14Hz, 1H, CH=), 9.58 (d, J = 12Hz, 1H, NH)
2c	3230 (NH), 2210 (CN)	4.67 (d, J = 14Hz, 1H, CH=), 6.86–7.62 (m, 3H, aromatic H), 7.92 (dd, J = 12Hz, J = 14Hz, 1H, CH=), 9.89 (d, J = 12Hz, 1H, NH)
2d	3310 (NH), 2200 (CN)	4.88 (d, J = 14Hz, 1H, CH=), 7.00–7.52 (m, 3H, aromatic H), 7.81 (dd, J = 12Hz, J = 14Hz, 1H, CH=), 9.62 (d, J = 12Hz, 1H, NH)
2e	3240 (NH), 2200 (CN)	4.63 (d, J = 15Hz, 1H, CH=), 7.02–7.57 (m, 3H, aromatic H), 8.04 (dd, J = 12Hz, J = 15Hz, 1H, CH=), 9.98 (d, J = 12Hz, 1H, NH)

This, however, affords an *E-Z* isomerisation either of **6** or of the primary condensation products. **7a** is reported in literature to show significant activity by inhibiting alcohol dehydrogenase in vitro [13].

Experimental Part

Melting points are uncorrected (Büchi-500). Spectral data were recorded with the following instruments: IR-spectra: Perkin Elmer Spectrophotometer 298 (KBr Pellets); ^{1}H-NMR spectra: Varian

Table 3. Reflux time, solvent of crystallization, yields, melting points, and elemental analysis of cyanoacetaldehydehydrazones **3a–e**

Compound	Reflux time (h)	Yield (%)	(Solvent)	M.p. (°C)	Elemental analysis		C	H	N
3a	24	90	(H_2O)	146	$C_5H_7N_3O_2$	calcd.	42.55	4.99	29.77
					(141.1)	found	42.65	5.00	30.05
3b	4	95	(H_2O)	122	$C_6H_9N_3O_2$	calcd.	46.44	5.84	27.08
					(155.2)	found	46.12	5.82	27.04
3c	6	93	($CHCl_3$)	170–172	$C_9H_7N_5O_4$	calcd.	43.38	2.83	28.10
				(Ref. [15]: 170–171)	(249.2)	found	43.12	2.99	28.09
3d	24	80	($CHCl_3$)	141–143	$C_{10}H_8ClN_3O$	calcd.	54.18	3.63	18.95
					(196.6)	found	53.98	3.68	18.11
3e	24	84	($CHCl_3$)	139	$C_9H_8N_4O$	calcd.	57.44	4.28	29.77
					(212.2)	found	57.22	4.43	29.71

Table 4. IR and NMR data of cyanoacetaldehydehydrazones **3a**, **3b**, **3d**, and **3e**

Compound	IR ν(cm^{-1})	^{1}H-NMR (*DMSO-d_6*) δ (ppm)
3a	3285 (NH), 2260 (CN), 1720 (C=O)	3.60 (d, J = 3.5 Hz, 2H, CH_2), 3.68 (s, 3H, $-CH_3$), 7.30 (t, J = 3.5Hz, 1H, –CH=), 11.1 (s, 1H, NH)
3b	3250 (NH), 2260 (CN), 1700 (C=O)	1.32 (t, 3H, $-CH_3$), 3.43 (d, J = 3.5Hz, 2H, $-CH_2$), 4.28 (q, 2H, $-CH_2$), 7.45 (t, J = 3.5Hz, 1H, –CH=), 8.23 (s, 1H, NH)
3d	3250 (NH), 2250 (CN), 1710 (C=O)	3.65 (d, J = 3.5Hz, 2H, $-CH_2$), 7.20–8.05 (m, 5H, –CH=, aromatic H), 11.50 (s, 1H, NH)
3e	3250 (NH), 2250 (CN), 1700 (C=O)	3.75 (d, J = 4Hz, 2H, CH_2), 7.20–9.20 (m, 5H, –CH=, aromatic H), 11.60 (s, 1H, NH)

360 AM and Gemini 200 (references on tetramethylsilane); Ozone was generated using a Fischer instrument 503.

Cyanoacetaldehyde **(1)** was freshly prepared by ozonization of (*E*)-1,4-dicyano-2-butene (38 mmol) or allylcyanide (76 mmol) in dichloromethane-methanol [2].

General Procedure for the Condensation Products With Anilines **(2a–e)**

To a freshly prepared solution of **1** (38 mmol) aniline (38 mmol) was added and stirred at 40 °C for 2 h. The solvents were removed under reduced pressure, the residue was treated with water (40 ml) and

ethanol (10 ml) and recrystallized from C_2H_5OH/H_2O. For elemental analysis see Table 1 and for spectroscopic data Table 2.

General Procedure for the Preparation of the Hydrazones **3a–e**

To a freshly prepared solution of **1** (38 mmol) the corresponding hydrazine (38 mmol) was added and the mixture was stirred at r.t. or refluxed for the time given in the Table 3. The solvents were removed under reduced pressure and the residue recrystallized from ethanol. For spectroscopic data see Table 4.

5-Amino-1-methoxycarbonylpyrazole (**4a**)

To a solution of **3a** (3.55 g, 25 mmol) in acetonitrile (30 ml) triethylamine (5 ml, 50 mmol) was added and the mixture was refluxed for 6 h. The solvent was removed under reduced pressure. Colourless needles 78% (ethanol), m.p. 130 °C. $C_5H_7N_3O_2$ (141.1): calcd. C 42.55, H 4.99, N 29.77; found C 42.83, H 5.01, N 30.12.

5-Amino-1-ethoxycarbonylpyrazole (**4b**)

Similar to the above procedure **3b** (3.88 g, 25 mmol) was refluxed for 24 h. 62% (CH_2Cl_2), m.p. 144–45 °C. $C_6H_9N_3O_2$ (155.2): calcd. C 46.44, H 5.80, N 27.02; found C 46.79, H 5.50, N 26.85.

5-Amino-1-(2,4-dinitrophenyl)-pyrazole (**4c**)

To a solution of **3c** (3.12 g, 12.5 mmol) in methanol (25 ml), methanolic KOH (1.5 ml, 2%) was added

Table 5. IR and NMR data of 5-aminopyrazoles **4a–d**

Compound	IR $\nu(cm^{-1})$	^{1}H-NMR (*DMSO-d_6*) δ(ppm)
4a	3450 (NH_2), 1740 (C=O)	3.88 (s, 3H, $-OCH_3$), 5.52 (s, 2H, $-NH_2$), 5.85 (d, $J = 2.5$Hz, 1H, aromatic H), 7.93 (d, $J = 2.5$Hz, 1H, aromatic H)
4b	3470 (NH_2), 1720 (C=O)	1.30 (t, 3H, $-CH_3$), 4.30 (q, 2H, CH_2), 5.50 (bs, 2H, NH_2), 5.83 (d, $J = 2.5$Hz, 1H, aromatic H), 7.91 (d, $J = 2.5$Hz, 1H, aromatic H)
4c	3400 (NH_2)	5.25 (bs, 2H, NH_2), 5.65 (d, $J = 2.5$Hz, 1H, aromatic H), 7.39 (d, $J = 2.5$Hz, 1H, aromatic H), 8.07 (d, $J = 5$Hz, 1H, aromatic H), 8.55 (dd, $J_{om} = 2.5$, 5.0Hz, 1H, aromatic H), 8.75 (d, $J_m = 2.5$Hz, 1H, aromatic H)
4d	3330 (NH_2), 3160 (bs, OH)	3.25–4.02 (m, 4H, CH_2CH_2), 5.00 (bs, 2H, NH_2), 5.28 (d, $J = 2.5$Hz, 1H, aromatic H), 7.05 (d, $J = 2.5$Hz, 1H, aromatic H)

and refluxed for 8 h. The solvent was removed under reduced pressure and the residue treated with water (10 ml); 60% (benzene), m.p. 135–37 °C. $C_9H_7N_5O_4$ (249.2): calcd. C 43.38, H 2.83, N 28.11; found C 43.12, H 2.98, N 27.96.

5-Amino-1-(2-hydroxyethyl)-pyrazole (**4d**)

To a freshly prepared solution of **1** (2.6 g, 38 mmol), 2-hydroxyethylhydrazine (2.8 g, 36 mmol) was added and the mixture refluxed for 4 h. The solvents were removed under reduced pressure to obtain a solid. 60% ($CHCl_3$), m.p. 99–101 °C. $C_5H_9N_3O$ (127.1): calc. C 47.20, H 7.15, N 33.02; found C 47.03, H 7.22, N 32.91.

For spectroscopic data of **4a–d** see Table 5.

Sodium 2,4-dicyano-1,3-butadiene-1-olate (**5a**)

Phenol (3.6 g, 38 mmol) was added to a solution of sodium (0.87 g) in ethanol (12 ml), mixed with a freshly prepared solution of **1** (38 mmol) and stirred at 50 °C for 1 h. The solvents were removed under reduced pressure, the residue was treated with ether (40 ml) and acetonitrile (10 ml) and filtered. 60%, IR: $\nu = 2210\,cm^{-1}$. ^1H-NMR (*DMSO-d_6*): $\delta = 4.34$ (d, $J = 16Hz$, 1H, CH=), 7.15 (d, $J = 16Hz$, 1H, CH=), 8.66 (s, 1H, CH=) ppm. $C_6H_3N_2Na \cdot 2H_2O$ (178.1): calcd. C 40.01, H 2.83, N 15.73; found C 41.44, H 2.83, N 15.54.

Table 6. Reflux time, yields, melting points and elemental analysis of 4-cyanopyrazoles **7a–k**

Compound	Reflux time (min)	Yield (%)	M.p. (°C)	Elemental analysis		C	H	N
7a	60	55	89–90	$C_4H_3N_3$	calcd.	51.61	3.24	45.14
			(Ref. [7]: 90–91)	(93.0)	found	51.65	3.40	45.26
7b	120	60	57–59	$C_5H_5N_3$	calcd.	56.06	4.70	39.22
			(Ref. [16]: 57–59)	(107.1)	found	55.30	5.13	39.21
7c	30	64	78	$C_6H_7N_3O$	calcd.	52.54	5.14	30.64
				(137.1)	found	55.48	4.97	30.60
7d	90	68	89–91	$C_8H_{11}N_3$	calcd.	63.07	7.35	27.74
				(149.2)	found	63.22	7.38	27.87
7e	30	79	99–100	$C_6H_5N_3O_2$	calcd.	47.68	3.33	27.80
				(151.1)	found	47.52	3.45	27.70
7f	40	78	81–82	$C_7H_7N_3O_2$	calcd.	50.89	4.27	25.47
				(165.1)	found	50.81	4.37	25.37
7g	30	55	194–195	$C_5H_4N_4O$	calcd.	44.12	2.96	41.16
				(122.1)	found	44.02	3.07	41.30
7h	45	63	164–165	$C_5H_4N_4S$	calcd.	39.46	2.64	36.81
				(136.1)	found	39.34	2.78	36.92
7i	60	82	92	$C_{10}H_7N_3$	calcd.	70.99	4.17	24.84
			(Ref. [17]: 95)	(169.2)	found	70.84	4.21	24.78
7j	30	81	128	$C_{11}H_9N_3$	calcd.	72.11	4.95	22.93
			(Ref. [18]: 128–130)	(183.2)	found	72.04	4.84	22.63
7k	60	65	194	$C_{10}H_6N_4O_2$	calcd.	56.07	2.82	26.15
			(Ref. [19]: 191–192)	(214.2)	found	55.85	2.93	26.16

4-Hydroxy-1,3-butadiene-1,3-dicarbonitrile (**5b**)

Hydrochloric acid (5 ml, 50%) was added to **5a** (1.0 g), stirred at r.t. for 20 min and filtered, 75% (water), m.p. 98–100 °C. IR: $\nu = 2800$–3400, 2240, 2220 cm^{-1}: ^{1}H-NMR (*DMSO-d_6*): $\delta = 5.41$ (d, $J = 16$Hz, 1H, CH=), 7.43 (d, $J = 16$Hz, 1H, CH=), 8.13 (s, 1H, OH), 8.80 (s, 1H, OH) ppm. $C_6H_4N_2O$ (120.1): calcd. C 60.00, H 3.36, N 23.33; found C 59.23, H 3.40, N 22.59.

4-Benzoyloxy-1,3-butadiene-1,3-dicarbonitrile (**5c**)

To a solution of **5a** (0.2 g, 1.1 mmol) in water (2 ml) benzoylchloride (0.3 g, 2.1 mmol) in CH_2Cl_2 (1.0 ml) was added, the *pH* adjusted to 8 with NaOH (5 ml, 25%) and stirred vigorously at r.t. for 1 h. After addition of CH_2Cl_2 (5 ml) the organic layer was separated, the solvent was removed under reduced pressure to get the solid, 81% (water), m.p. 124–26 °C. IR: $\nu = 3070$, 2220, 1755, 1635 cm^{-1}; ^{1}H-NMR (*DMSO-d_6*): 5.97 (d, $J = 16$Hz, 1H, CH=), 7.20 (d, $J = 16$Hz, 1H, CH =), 7.50–8.46 (m, aromatic H), 8.57 (s, 1H, CH=) ppm.

3-Dimethylamino-2-formylpropenenitrile (**6**)

To a freshly prepared solution of **1** (2.6 g, 38 mmol) dimethylformamide-dimethylacetal (6.5 g, 54 mmol) was added and stirred at r.t. for 1 h. The solvents were removed under reduced pressure to get the solid. 65% (ethanol), m.p. 138 °C (Ref. [9]: 141 °C). ^{1}H-NMR: ($CDCl_3$): $\delta = 3.28$ (s, CH_3), 3.32 (s, CH_3), 7.84 (s, 1H), 9.07 (s, 1H).

Table 7. IR and NMR data of 4-cyanopyrazoles **7c–h**

Compound	IR ν (cm^{-1})	^{1}H-NMR (*DMSO-d_6*) δ (ppm)
7c	3370 (–OH), 2240 (CN)	3.73 (q, $J = 5.0$Hz, $-CH_2$), 4.22 (t, $J = 5.0$Hz, 2H, $-CH_2$), 4.98 (t, $J = 5.0$Hz, 1H, –OH), 8.05 (s, 1H, aromatic H), 8.55 (s, 1H, aromatic H)
7d	2230 (CN)	1.55 (s, 9H, *t*-butyl), 8.07 (s, 1H, aromatic H), 8.69 (s, 1H, aromatic H)
7e	2240 (CN), 1770 (C=O)	4.10 (s, 3H, $-OCH_3$), 8.43 (s, 1H, aromatic H), 9.31 (s, 1H, aromatic H)
7f	2240 (CN), 1770 (C=O)	1.38 (t, 3H, $-CH_3$), 4.50 (q, 2H, $-CH_2$), 8.39 (s, 1H, aromatic H), 9.28 (s, 1H, aromatic H)
7g	3400 (NH_2), 2230 (CN), 1750 (C=O)	8.20 (s, 2H, NH_2), 8.32 (s, 1H, aromatic H), 9.12 (s, 1H, aromatic H)
7h	3360 (NH_2), 2240 (CN)	8.45 (s, 1H, aromatic H), 9.45 (s, 1H, aromatic H), 9.85 and 10.42 (s, 1H, NH_2)

General Procedure for the Preparation of 4-Cyanopyrazoles **7a–k**

To a solution of **6** (10 mmol) in ethanol (25 ml) and conc. HCl (1.2 ml) (for **7a–h** and **7j**) resp. acetic acid (5 ml) (for **7i** and **7k**), the corresponding hydrazine (10 mmol) was added and refluxed for the time given in Table 6. The solvent was removed under reduced pressure and the residue recrystallized from ethanol. For spectroscopic data of **7c–h** see Table 7.

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