



Title	Reactions of Malononitrile under Hydrogen Pressure
Author(s)	YANAGIMACHI, Harumitsu; KASHIKI, Isamu; SAKAI, Makoto; SUZUKI, Akira; MIKI, Masayuki
Citation	北海道大學水産學部研究彙報, 29(2), 188-194
Issue Date	1978-06
Doc URL	http://hdl.handle.net/2115/23645
Type	bulletin (article)
File Information	29(2)_P188-194.pdf



[Instructions for use](#)

*in vivo*¹⁴), and the incorporation *in vitro* of uridine into the RNA of dipteran salivary glands¹⁵), and the related area¹⁶). On the other hand, the trimer may be of interest as a most readily available pyrazole.

An exploration of catalysts revealed that both hydrogen and catalyst(s) were necessary to promote the polymerization, and Pd, Pt, Rh, Cu, Ni and Co, had excellent activity in that order and the rate of the reaction was well within commercial feasibility.

Experimental Section

Raw material and catalyst Malononitrile (extra reagent grade), Pt-I (5% Pt on activated C), Pt-II (0.5% Pt on alumina), Pd-I (5% Pd on activated C), Pd-II (0.5% Pd on alumina), Rh (5% Rh on activated C), Ru (5% Ru on activated C), Ni (5% Ni on activated C), Co (5% Co on activated C), Cu (CuCO₃·Cu(OH)₂·H₂O), Mn (MnCl₂·4H₂O), V (V₂O₃), Zn (ZnCO₃), Hg (HgCl₂·2H₂O), Cr ((NH₄)₃CrO₄), Cd (CdCO₃), Ir (Ir₂O₃), Os (OsO₄), Ag (10% Ag on alumina), Fe (neutralization of ferrous sulfate with aq. NH₃ followed by heat treatment at 200°C), Mo (5% Mo on alumina).

Chemical states in action are ambiguous except for Pt, Pd, Rh, Ni and Co (metal), Cr, Mo and V (metal oxide). Those of Zn, Cd and Hg are supposed to be salts. Zn salt has been used as a catalyst for coal hydrogenation.

Procedure In an autoclave, 16 mm in dia. and 20 ml in vol. were placed 5 g of malononitrile (except for Run 7 where 10 g was used), a specified amount of catalyst and a steel ball for agitation, and hydrogen was introduced up to a specified pressure (initial pressure) of 50 kg/cm². The reactor was then immersed in an oil bath held at a prescribed temperature (reaction temperature) and shaken violently at 200 r.p.m. for a prescribed period of time, and quenched immediately with cold water. It took about four min to arrive at the reaction temperature after immersion, so the reaction time was subtracted by that amount from the prescribed value. The knocking sounds of the ball disclosed an approximate progress of the reaction, which ceased at about 70% conversion. The products were solids even at the reaction condition, fractional distillation being used for separation. The fractions obtained were unreacted malononitrile (up to 70°C at 15 mm Hg), Distillate I (following fraction up to 150°C at 2 mm Hg), Distillate II (last fraction up to 250°C at 2 mm Hg). Carbonaceous material in an amount of less than 5% was left as residue.

Analysis Elemental analyses, MS, UV, IR, ¹H NMR and ¹³C NMR were used for identification.

Results and Discussion

The elemental analyses and necessary spectroscopic data for identification appear in Table 1.

Distillate I Recrystallization from water yielded pale yellow crystals, m.p. 170–171°C. The elemental analysis and MS show it is a dimer. The UV, IR and ¹H NMR support the structure, 1,1,3-tricyano-2-amino-1-propene. Chemical intuition suggests its formation by a Thorpe type reaction. Past investigators^{4), 5), 6), 7), 8)} unanimously supported the structure. Nevertheless, the ¹³C NMR

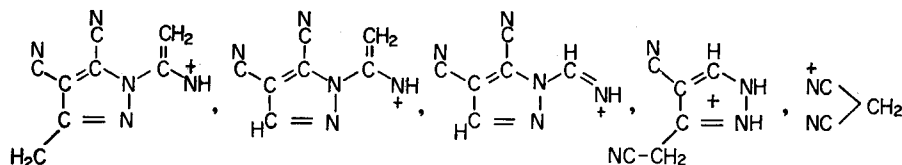
Table 1. Data used for identification

Item	Distillate I	Distillate II
Elemental analysis (%): ^{a)}		
C	54.8 (54.5)	54.8 (54.5)
H	3.1 (3.1)	3.0 (3.1)
N	40.1 (42.4)	40.6 (42.4)
MS (80 eV, m/e):	M ⁺ 132 (50)	M ⁺ 198 (100)
	92 (100) ^{b)}	171 (7) ^{c)}
	66 (50) ^{b)}	158 (5) ^{c)}
	41 (100) ^{b)}	144 (10) ^{c)}
		133 (4) ^{c)}
		66 (5) ^{c)}
UV (nm)	275 (EtOH)	242 (pH 2)
		252 (pH 12)
IR (cm ⁻¹)	3320 s } (ν NH ₂)	3340 s } (ν NH ₂)
	3200 s } (ν NH ₂)	3260 s } (ν NH ₂)
	2960 w } (-CH ₂ -)	3180 s } (-CH ₂ - & =CH ₂)
	2900 s } (-CH ₂ -)	3110 s } (-CH ₂ - & =CH ₂)
	2260 w unconj. CN	2240 w unconj. CN
	2220 s conj. CN	2200 s conj. CN
	2200 s conj. CN	2200 s conj. CN
¹ H NMR (DMSO-d ₆ , τ -value)	s, 1.12 (-NH ₂)	s, 2.60 (-NH ₂)
	s, 6.22 (-CH ₂ -)	s, 2.78 (=CH ₂)
		s, 6.72 (-CH ₂ -)
¹³ C NMR (DMSO-d ₆ , ppm)	22 (-CH ₂ -)	26 (-CH ₂ -)
	50 (-C=)	71 (=CH ₂)
	114 (-CN)	81 (-C=)
	114.5 (-CN)	113 (-CN)
	115 (-CN)	113.5 (-CN)
	165 (=C-NH ₂) ?	114.5 (-CN)
		156 (aromatic)
		156.5 (aromatic)
		159 (aromatic)

a) Figures in the parentheses are based on [CH₂(CN)₂].

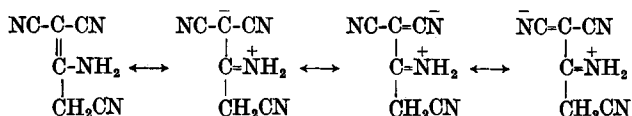
b) The mass peaks can be assigned to [(NC)₂=CNH₂]⁺, [(NC)₂CH₂]⁺ and [CH₂CNH]⁺, respectively.

c) These can be assigned to the following fragments, respectively.



resonance peak at 165 ppm, which is located too downfield to be assigned to =C-NH₂ raises a question which is worth further comments. Matsumoto¹⁷⁾ showed that the proton chemical shifts of malononitrile were dependent heavily upon solvents used (209.2 cps for CCl₄, 264.4 cps for DMSO). It seems quite probable that similar solvent effects act upon the dimer. On the other hand, Eberts¹⁸⁾ explained the large proton chemical shift of the dimer located at 1.12 τ by assuming the

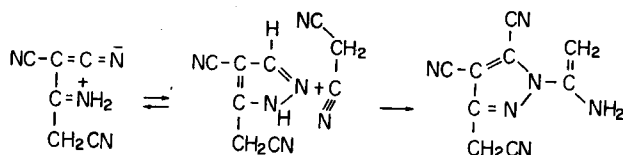
following resonance-stabilized zwitterionic forms.



Here the resonance stabilization seems to contribute to reduce the electron density around the C atom. This, together with the solvent effect, may lead to the incredibly large ^{13}C chemical shift.

Distillate II Recrystallization from dioxane gave white powder, which, upon heating, underwent indefinite decomposition above 290°C . The elemental analysis and MS show it is a trimer of malononitrile. The ^{13}C NMR and the strong intensity of the molecule ion MS suggest it has three aromatic C atoms. The IR and ^{13}C NMR indicate it has three nitrile groups including conjugated and unconjugated ones. The IR, ^1H NMR and ^{13}C NMR support existence of an amino group and a methylene group. The remaining two N atoms and the three aromatic C atoms should be assigned to a diazole heterocycle. Further, the ^1H NMR, ^{13}C NMR, UV and IR suggest a 1-aminovinyl group. Total deuterizability also supports this idea.

Taking these informations and the following reaction scheme into consideration, we offer the structure, 1-(aminovinyl)-3-cyanomethyl-4,5-dicyano-pyrazole, for the trimer.



Schenk and Finken⁹⁾ obtained the trimer when they treated malononitrile and oxalic esters with sodium ethoxide or diethylamine, and suggested the structure, either 2,6-dicyanomethyl-4-amino-5-cyano-pyridine or 2,4,6-tricyanomethyl-triazine. Anderson et al.¹⁰⁾ traced the experiment and inferred the structure, 1,1,3,5-tetracyano-2,4-diamino-3-pentene (using IR). Junek and Sterk¹¹⁾ prepared the trimer by the treatment of malononitrile with piperidine in ethanol and identified it as 1,4-dicyano-2,5-diamino-3-imino-cyclopentadieno-(3,2-b)-pyrrole (using MS, IR and ^1H NMR). Taguchi and Matsuura¹²⁾ treated malononitrile in an aqueous alkaline solution and obtained the trimer, which they identified as 1,1,3-tricyano-6-cyanomethyl-pyridine (using MS, IR and ^1H NMR). Finally, Kawabata et al.¹³⁾ treated malononitrile with cuprous chloride and pyridine and obtained the compound for which they gave a polymer structure consisting of $-\text{C}(\text{CN})=\text{C}(\text{NH}_2)_n-$ and $-\text{CH}(\text{CN})-\text{C}(=\text{NH})_n-$ (using IR and ^1H NMR). As was seen, all the past investigators did not have sufficient analytical data, and consequently, their conclusions were incorrect.

Table 2. Summary of the experimental results

Run no.	Catalyst			Reaction temp. °C	Reaction time min	Conversion %	Activity %/min/4 mg-cat
	Name	Wt. incl. carrier mg	Net wt. mg				
1	None	0	0	140	120	0	0
2	Act. C	20	20	140	120	0	0
3	Al ₂ O ₃	20	20	140	120	0	0
4* ¹	Pt-II	20	0.4	140	120	0	0
5* ²	Pt-II	20	0.4	140	120	0	0
6* ²	Pt-II	20	0.4	140	360	42	0.12
7* ³	Pt-II	20	0.4	140	90	62	0.78
8	Pt-II	20	0.4	135	30	44	1.5
9	Pt-I	20	4	135	13	36	2.8
10	Pd-II	20	0.4	135	10	65	65
11	Pd-I	20	4	135	5	60	12
12	Mo	10	2	130	120	26	0.86
13	Cu	10	10	135	5	52	4.16
14	Mn	20	20	135	95	25	0.06
15	V	20	20	135	90	0	0
16	Zn	20	20	135	20	43	0.5
17	Cr	20	20	135	90	28	0.07
18	Fe	10	10	135	90	41	0.18
19	Co	10	2	135	50	37	1.48
20	Ni	10	2	135	30	29	2.00
21	Ru	10	2	135	90	26	0.58
22	Rh	10	2	135	13	47	7.20
23	Os	10	10	135	90	0	0
24	Ir	10	10	135	90	0	0
25	Ag	20	2	135	0	0	0
26	Cd	20	20	135	90	80	0.19
27	Hg	20	20	135	80	40	0.12

Five g of nitrile was used except Run 7 (10 g). Initial hydrogen pressure was always 50 kg/cm².

*¹ Fifty kg/cm² of nitrogen was used instead of hydrogen.

*² Fifty kg/cm² of helium was used instead of hydrogen.

*³ Fifty kg/cm² of deuterium was used instead of hydrogen.

Reaction

Reactions of malononitrile with or without a catalyst are as shown in Table 2. Since the pressure of the gas after the reaction and the subsequent quenching (final pressure) was always equal to the initial pressure and the gas contained no foreign substances other than hydrogen, no mention was made about them.

As will be written elsewhere, the reaction can be approximated as zero order with respect to malononitrile and first order with respect to catalyst, and the temperature dependency of the reaction rate is shown as 20 kcal/mole expressed in apparent activation energy. A rough comparison of catalyst activities is shown in the last column in a unit of percent conversion per min per 4 mg of catalyst.

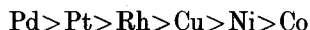
The reaction hardly took place in the atmosphere of nitrogen and helium, as can be seen from Runs 3, 4 and 5, and the presence of hydrogen appears essential to

promote the reaction.

Even in the presence of hydrogen, no reaction took place without a catalyst or with the mere use of activated carbon or alumina which was used as the catalyst carrier (Runs 1, 2, 3).

However, with the presence of hydrogen and the so-called hydrogenation catalyst, the reaction did occur. Unexpectedly, it was not the hydrogenation but the polymerization that yielded exclusively the dimer and the trimer.

The activity of the catalysts is put in the following order.



Salts of Zn, Cd and Hg showed very weak activity. In view of Kawabata and Yamashita's report¹³ showing that Cu_2Cl_2 with triethylamine had catalytic activity in the absence of hydrogen, it is probable that they function differently from the metal catalysts.

When deuterium was used instead of hydrogen, the reaction arose (Run 7), however, the resultant dimer and trimer contained no deuterium, which will throw some light on the mechanism of the reaction.

The kinetics of the reaction by the use of a Pt catalyst will be dealt with in the following paper.

References

- 1) Tarama, K. (1971). *Classification of catalysts by type of reaction, I*. Kagaku Kogyo Sha, 18-19.
- 2) Tarama, K. (1972). *Classification of catalysts by type of reaction, II*. Kagaku Kogyo Sha, 24-25.
- 3) Freifelder, M. (1971). *Practical Catalytic hydrogenation*. Wiley-Interscience, 247-249.
- 4) Meier, R. (1953). Reaction of metalloorganic compounds with nitrous oxide. *Chem. Ber.* **86**, 1483-1493.
- 5) Carboni, R.A. (1958). Cyanocarbon chemistry. XI. Malonitrile dimer. *J. Am. Chem. Soc.* **80**, 2838-2840.
- 6) Taylor, E.C. (1959). The reaction of malonitrile with hydrazine. *Ibid.* **81**, 2452-2455.
- 7) Decombe, J. and Verry, C. (1963). Dimerization of dinitriles in anhydrous hydrochloric acid. *Compt. Rend.* **256**, 5156-5158.
- 8) Takahashi, K., Miyake, A. and Hata, G. (1971). Dimerization of malonitrile by palladium and platinum complex catalysts. *Bull. Chem. Soc. Jap.* **44**, 3484-3485.
- 9) Schenk, R. and Finken, H. (1928). Ueber Malonitril und Malonitrilkondensationen. II. *Ann. Chem.* **462**, 267-283.
- 10) Anderson, D.M.W., Bell, F. and Duncan, J.L. (1961). Some condensation products of malonitrile. *J. Chem. Soc.*, 4705-4711.
- 11) Junek, H. and Sterk, H. (1967). Zur Struktur der trimeren Malonsäurenitrile. *Z. Naturforsch.* **22**, 732-734.
- 12) Taguchi, M. and Matsuura, K. (1969). Trimers of malonitrile. *J. Syn. Org. Chem. Jap.* **27**, 1230-1234.
- 13) Kawabata, N., Chen, C.K. and Yamashita, S. (1972). Hydrogen transfer polymerization of malonitrile. *Bull. Chem. Soc. Jap.* **45**, 1491-1493.
- 14) Egyhazi, E. and Hyden, H. (1961). Experimentally induced changes in the base composition of the ribonucleic acids of isolated nerve cells and their oligodendroglial cells. *J. Biophys. Biochem. Cytol.* **10**, 403-410.
- 15) Jacob, J. and Sirin, J.L. (1964). Synthesis of RNA in vitro stimulated in dipteran

- salivary glands by 1,1,3-tricyano-2-amino-propene. *Science* 144, 1011-1012.
- 16) Dingman, W and Sporn M.B. (1964). Molecular theories of memories. *Ibid.* 144, 26-29.
 - 17) Matsuo, T. and Kodera, Y. (1966). Solvent effects in the proton chemical shifts of acetonitrile and malononitrile. *J. Phys. Chem.* 70, 4087-4089.
 - 18) Eberts, Jr., F.S., Slomp, G. and Johnson, J.L. (1961). 1,1,3-Tricyano-2-amino-1-propene, a biologically active component of aqueous solutions of malononitrile. *Arch. Biochem. Biophys.* 95, 305-309.