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Anomalous Reaction of Arylmalononitriles with Nitric Acid. Para-Directing Nature of Dicyanomethyl Group and a Through-Ring Nitro/*aci*-Nitro Tautomerism of 4-Nitrophenylmalononitrile¹⁾

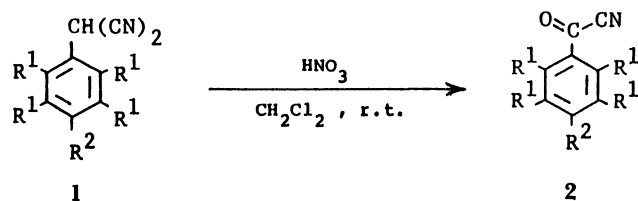
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Phenylmalononitrile reacts with nitric acid in dichloromethane at room temperature to afford 1,2-bis(4-nitrophenyl)-1,1,2,2-tetracyanoethane as an initial product, which readily suffers oxidative cleavage to give 4-nitrobenzoyl cyanide. Contrary to common understanding, dicyanomethyl group exhibits no meta-directing property. 4-Nitrophenylmalononitrile is found to exist in two stable tautomeric forms, which undergo a facile nitro/*aci*-nitro interconversion across aromatic ring depending on the nature of solvent employed.

Successive replacement of methyl hydrogen atoms in toluene by chlorine atoms changes the directing effect of methyl group from predominant ortho/para orientation to predominant meta orientation. Thus, benzyl chloride gives on nitration ortho, meta, and para nitro derivatives in 34, 14, and 53% yields, respectively,²⁾ while the value is 7, 65, and 29% respectively for benzylidene trichloride.³⁾ Since the cyano group is more strongly deactivating than chlorine atom, it is quite understandable that the substitution of two cyano groups into methyl group of toluene would change the directing nature of methyl group from ortho/para into meta. Indeed, Flürsheim and Holmes nitrated phenylmalononitrile (**1a**) with nitric acid in acetic anhydride and obtained 68 and 32% respectively of meta and (ortho plus para) nitration products.⁴⁾ Their result has been taken as one of the examples of the substituent-dependent modification of the electron-releasing property of methyl group and no doubts seem to have been thrown for more than half a century.

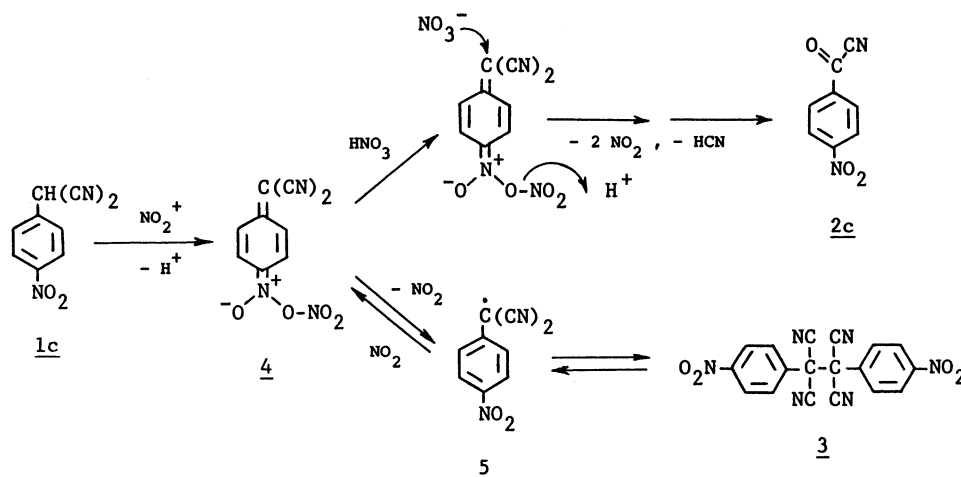


In the course of our continuing study on the non-conventional aromatic nitration,⁵⁾ we had an occasion to reinvestigate the reaction of several arylmalononitriles with nitric acid under various conditions. Rather surprisingly, dinitrile **1a** underwent a facile reaction both on aromatic ring and on side chain, giving 4-nitrobenzoyl cyanide (**2c**) in a good yield. In contrast to the literature report,⁴⁾ no 3-nitro isomer could be detected in the product mixture.

A close inspection of this unexpected result revealed a new chemistry. Thus, when the reaction was quenched with water immediately after the addition of nitrating agent to a solution of **1a** in dichloromethane at room temperature and the organic phase was worked up as usual, the product was a pale yellow

crystalline solid which, after several recrystallization from THF and ether, melted at 156–157°C with decomposition. On dissolving into THF and acetone, it developed a pale yellow and an orange color respectively. Its solution in DMSO had a deep red color. Elemental analysis of this compound was consistent with the empirical formula $C_{18}H_8N_6O_4$. The IR spectrum (KBr) demonstrated the presence of cyano (2275 cm^{-1}) and nitro groups (1535 and 1360 cm^{-1}), while its ¹H NMR spectrum (100 MHz; $(CD_3)_2SO$) showed signals at δ 8.50 and 7.70 (d; $J=9.6$ Hz), relative intensity 1:1, due to vicinal aromatic protons. The ¹³C NMR spectrum (90 MHz; $(CD_3)_2SO$) indicated the presence of cyano groups (δ 110.0), substituted aromatic carbons (δ 129.4 and 149.5), unsubstituted aromatic carbons (δ 124.6 and 130.0), and sp^3 carbons (δ 52.8). These spectral evidences allowed for the compound the formulation of 1,2-bis(4-nitrophenyl)-1,1,2,2-tetracyanoethane (**3**). Its structure was further confirmed by direct comparison with an authentic specimen obtained from the oxidation of 4-nitrophenylmalononitrile (**1c**) with yellow mercury(II) oxide in dichloromethane at room temperature. When kept in contact with nitric acid in the same solvent, **3** was converted into benzoyl cyanide **2c**. Under similar conditions, 4-methylphenylmalononitrile (**1b**) and 2,3,5,6-tetrachloro-4-methylphenylmalononitrile (**1d**) afforded the corresponding benzoyl cyanide **2b** and **2d** as the respective single product. Interestingly, dinitrile **1c** with two electron-withdrawing groups on aromatic ring reacted more easily with nitric acid than unsubstituted dinitrile **1a** or methyl-substituted dinitrile **1b** to produce **2c** in high yields.

We also carried out the nitration of **1a** according to the procedure given in the literature.⁴⁾ The reaction proceeded quite rapidly, giving after 30 min 58% of **2c** and 22% of 4-nitrobenzoic acid along with several minor products. No 3-nitro compounds could be obtained again. Although the reaction mechanism remains to be clarified, the oxidation of dinitrile **1c** to acyl cyanide **2c** most likely involves a nitrated *aci*-nitro compound **4**, which is formed via a $Se2'$ type process in which the attack of an electrophile occurs on the oxygen atom of nitro group with the loss of proton

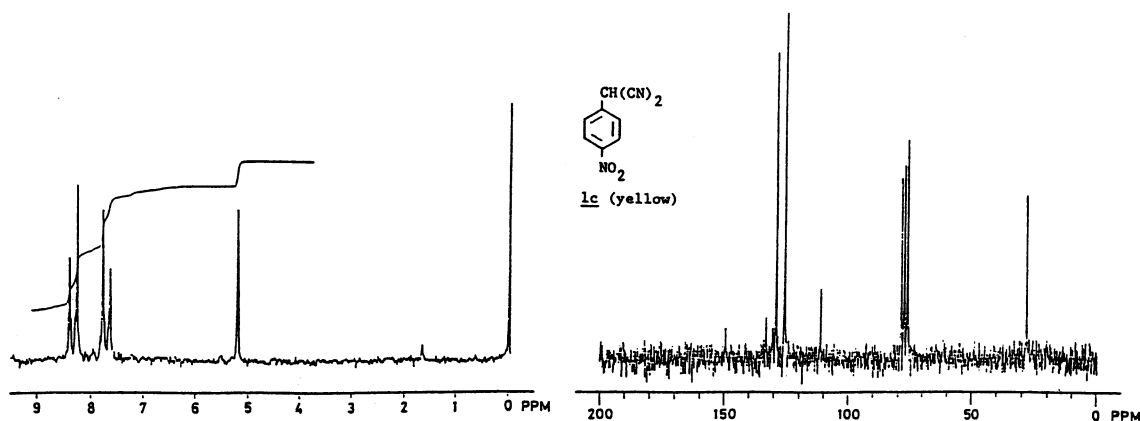


Scheme 1.

Table 1. Benzoyl Cyanides Obtained from the Reaction of Arylmalononitriles with Nitric Acid

	Arylmalononitrile 1		Reaction time/h	Benzoyl cyanide 2	
	R ¹	R ²		Mp (θ_m /°C)	Yield/% ^{a)}
a	H	H	6	116—117	77 ^{b)}
b	H	Me	8	50—51	74
c	H	NO ₂	0.7	116—117	85
d	Cl	Me	6	126—129	72

a) Yields refer to the isolated compounds and are not optimized. b) Product was 2c.

Fig. 1. ¹H and ¹³C NMR spectra of 1c in chloroform-d.

from the side chain. The intermediate **4** then undergoes attack of oxygen nucleophile on the electron-deficient exo-carbon to form acyl cyanide **2c** or dissociates into a radical **5** and nitrogen dioxide via the homolytic fission of a nitrogen-oxygen bond as sketched in Scheme 1. A stabilized radical **5** is expected to be in equilibrium with the dimer **3**.

Dinitrile **1c** is usually prepared by the action of cyanogen chloride on 4-nitrophenylacetone nitrile⁶⁾ or by the arylation of malononitrile anion with 4-bromonitrobenzene.⁷⁾ It is described as pale yellow plates melting at 109—110°C and characterized by its remarkable acidity.^{7,8)} When this compound was prepared by the literature method, there was obtained a pale yellow crystalline solid, mp 108.5—109.5°C. Its IR, ¹H and ¹³C NMR, and UV spectra were all consist-

Table 2. Spectroscopic Data of the Yellow and Red Forms of 4-Nitrophenylmalononitrile (2c)

 1c (yellow)	¹ H NMR (CDCl ₃): δ 5.21 (s, 1H), 7.76 (d, 2H; $J=8$ Hz), 8.40 (d, 2H; $J=8$ Hz)
	¹³ C NMR (CDCl ₃): δ 27.9 (CH), 110.6 (CN), 125.0 (CH), 128.5 (CH), 129.8 (C), 148.9 (C)
 6 (red)	IR (KBr): 2255, 1610, 1590, 1525, 1350, 855 cm ⁻¹ UV (CHCl ₃): λ_{max} 252 nm
	¹ H NMR (DMSO- <i>d</i> ₆): δ 6.81 (d, 2H; $J=9$ Hz), 7.18 (s, variable; 1H), 7.90 (d, 2H; $J=9$ Hz) ¹³ C NMR (DMSO- <i>d</i> ₆): δ 110.3 (CN), 119.5 (CH), 125.4 (CH), 130.3 (C), 138.0 (C), 149.3 (C)
	IR (KBr): 3340, 2190, 1520, 1345, 850 cm ⁻¹ UV (CHCl ₃): λ_{max} 222, 262, 459 (vs) nm

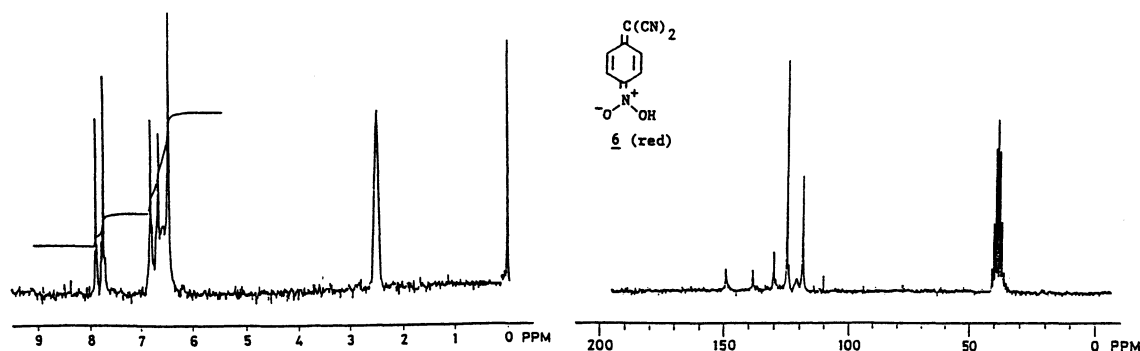


Fig. 2. ^1H and ^{13}C NMR spectra of **6** in $\text{DMSO}-d_6$.

ent with the aromatic structure **1c** (Table 2). When dissolved into methanol or DMSO, however, this yellow dinitrile developed a deep red color and the ^1H and ^{13}C NMR spectra of the solution thus obtained were completely different from those of chloroform or benzene solution (Figs. 1 and 2). A deep-colored methanolic solution was evaporated under reduced pressure to leave a dark red solid, which also exhibited an infrared spectrum very different from that of a pale yellow compound. The red dinitrile is soluble in acetone, DMSO, and methanol to form a red solution, but it is slightly soluble in benzene and chloroform to give a yellow solution. In contrast, the yellow dinitrile is soluble in most common organic solvents to give a yellow to deep red solution depending on the nature of solvent employed. Both dinitriles are interconvertible simply by choosing an appropriate solvent system. On the basis of spectroscopic and microanalytical data as well as their behaviors toward different solvent systems, a nitro structure **1c** was assigned to the yellow dinitrile and an *aci*-nitro structure **6** to the red one. Our finding represents an additional mode of nitro/*aci*-nitro tautomerism, which occurs through a long distance at the expense of aromatic stabilization of benzene nucleus.

Experimental

All melting points were determined on a hot-stage apparatus and are uncorrected. IR spectra were run as KBr pellets on a Hitachi 260-10 spectrophotometer and only prominent peaks are recorded. UV spectra were measured in chloroform with a Hitachi 220A spectrophotometer. ^1H and ^{13}C NMR spectra were obtained on Hitachi R-600 and JNM-FX-100 spectrometers using TMS as an internal standard. Unless otherwise stated NMR data refer to deuteriochloroform solutions. Mass spectra were determined on a Hitachi M-80B mass spectrometer with 70 eV ionizing current.

Arylmalononitriles were prepared by allowing the corresponding iodoarenes to react with malononitrile anion in the presence of copper(I) iodide in hot hexamethylphosphoric triamide (HMPA).⁹ The following typical example illustrates the general procedure used in the synthesis of the dinitriles. In the preparation of **1c**, assistance by copper(I) catalyst is not necessary.

2,3,5,6-Tetrachloro-4-methylphenylmalononitrile (1d). A commercial 60% sodium hydride dispersion in mineral oil (ca. 4 g) was washed three times by decantation with hexane and the remaining solid was covered with dry HMPA (10 ml). A solution of malononitrile (3.3 g) in the same solvent (10 ml) was added with stirring under nitrogen. After the cease of gas evolution, 2,3,5,6-tetrachloro-4-iodotoluene (3.56 g) was added, followed by copper(I) iodide (2.0 g), and the mixture was gradually heated to 85 °C and kept at this temperature for 10 h. TLC monitoring of the reaction mixture at this time showed no unreacted iodide. The black mixture was then quenched with dilute hydrochloric acid and the organic phase was extracted several times with ether. The extracts were combined, washed with aqueous sodium sulfite, and evaporated under reduced pressure. The crude product was chromatographed on silica gel using a hexane-dichloromethane mixture as eluent to give dinitrile **1d** as a crystalline solid, mp 207–209 °C. Yield, 1.65 g (56%). MS (70 eV) m/z (rel intensity) 293 (M^+ , 100), 264 (36), and 258 (37); ^1H NMR: δ =2.66 (s, 3H) and 6.11 (s, 1H); ^{13}C NMR: δ =20.67, 25.97, 109.20, 131.57, 132.22, 134.27, and 140.96; IR: 2240, 1550, 1440, 1400, 1385, 1360, 1135, and 1000 cm^{-1} . Found: C, 41.09; H, 1.39; N, 9.59%. Calcd for $\text{C}_{10}\text{H}_4\text{N}_2\text{Cl}_4$: C, 40.86; H, 1.37; N, 9.53%.

Phenylmalononitrile (1a): Mp 67–68 °C. ^1H NMR: δ =5.06 (s, 1H) and 7.48 (s, 5H); IR: 2250, 1490, 1450, 1010, 910, and 725 cm^{-1} .¹⁰

4-Methylphenylmalononitrile (1b): Mp 57–58 °C. ^1H NMR: δ =2.39 (s, 3H), 4.93 (s, 1H), and 7.0–7.2 (m, 4H); IR: 2250, 1500, 1005, 805, and 755 cm^{-1} . Found: C, 77.19; H, 5.11; N, 18.22%. Calcd for $\text{C}_{10}\text{H}_8\text{N}_2$: C, 76.90; H, 5.16; N, 17.94%.

4-Nitrophenylmalononitrile (1c): Mp 109–110 °C. ^1H NMR: δ =5.21 (s, 1H), 7.76 (d, 2H; J =8 Hz), and 8.40 (d, 2H; J =8 Hz); IR: 2255, 1610, 1590, 1525, and 1350 cm^{-1} . Found: C, 57.81; H, 2.45; N, 22.33%. Calcd for $\text{C}_9\text{H}_5\text{N}_3\text{O}_2$: C, 57.76; H, 2.69; N, 22.45%.⁶

Reaction of Arylmalononitriles with Nitric Acid. The procedure used in each of the reactions described was identical; therefore, only a typical example of these reactions will be reported in detail. The results are summarized in Table 1.

To a solution of 4-methylphenylmalononitrile (**1b**; 0.156 g) in dichloromethane (1 ml), nitric acid ($d=1.5$; 0.5 ml) was added and the mixture was stirred at room temperature for several hours, during the course of which the initial slightly yellow color gradually deepened to yellowish green, then faded to light yellow after 5 h. Liberation of nitrogen dioxide was observed. The mixture was diluted with water and the resulting turbid solution was extracted with dichloro-

methane. The extract was washed three times with cold water, dried with sodium sulfate, and evaporated under reduced pressure to leave a pale yellow solid. The residue was recrystallized from hexane-chloroform to afford 4-methylbenzoyl cyanide (**2b**) as colorless needles, mp 50–51 °C. Yield, 0.108 g (74%). ¹H NMR: δ=2.49 (s, 3H), 7.40 (d, 2H; *J*=8 Hz), and 8.05 (d, 2H; *J*=8 Hz); IR: 2215, 1660, 1595, 1260, and 975 cm⁻¹. Found: C, 74.18; H, 4.89; N, 9.66%. Calcd for C₉H₇NO: C, 74.47; H, 4.86; N, 9.65%.

On heating with methanol, **2b** was converted into methyl 4-methylbenzoate, identical with an authentic sample.

4-Nitrobenzoyl Cyanide (2c): Mp 116–117 °C. ¹H NMR: δ=8.41 (br. s, 2H) and 8.43 (br. s, 2H); IR: 2215, 1680, 1525, 1345, and 1230 cm⁻¹. Found: C, 54.64; H, 2.29; N, 15.71%. Calcd for C₈H₄N₂O₃: C, 54.55, H, 2.29; N, 15.90%.

2,3,5,6-Tetrachloro-4-methylbenzoyl Cyanide (2d): Mp 126–129 °C. ¹H NMR: δ=2.63 (s, 3H); IR: 2200, 1700, 1540, 1350, 1340, 1240, 1160, 1055, and 920 cm⁻¹. Found: C, 38.03; H, 1.09; N, 4.71%. Calcd for C₉H₃NOCl₄: C, 38.20; H, 1.07; N, 4.95%.

Oxidative Coupling of 4-Nitrophenylmalononitrile to 1,2-Bis(4-nitrophenyl)-1,1,2,2-tetracyanoethane. A solution of dinitrile **1c** in dichloromethane was mixed with nitric acid and the green reaction mixture obtained was quenched with iced water after a few minutes. A pale yellow solid was collected by filtration and fractionally crystallized from tetrahydrofuran-ether. Mp 156–157 °C. Found: C, 58.06; H,

2.03; N, 22.27%. Calcd for C₁₈H₈N₆O₄: C, 58.07; H, 2.17; N, 22.57%.

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