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Nitration of moderately deactivated arenes with nitrogen dioxide and molecular oxygen under neutral conditions. Zeolite-induced enhancement of regioselectivity and reversal of isomer ratios

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In the presence of zeolites, moderately deactivated arenes such as 1-nitronaphthalene, naphthonitriles, and methylated benzonitriles can be smoothly nitrated at room temperature by the combined action of nitrogen dioxide and molecular oxygen. The regioselectivity is considerably improved as compared with the conventional nitration methodology based on nitric and sulfuric acids. In some cases, the minor isomer became favoured to a significant extent, resulting in the reversal of ordinary isomer ratios of nitration products.

Introduction

In recent years, there has been a growing worldwide concern over the adverse effect of chemical wastes that arise from industrial activities. With regard to this, aromatic nitration is quite notorious for its unfriendly nature towards the environment.[1] The use of large quantities of nitric and sulfuric acids, corrosiveness, potential danger of explosion, low regioselectivity, oxidative degradation byproducts, and inefficient atomic economy all constitute the disadvantages of this time-honored reaction. Among a number of recent efforts to develop alternative methodologies, the combined use of nitrogen oxides (NO and NO_2) and oxygen in place of the classical nitric acid–sulfuric acid system appears to be the most attractive and promising. As everybody knows, commercial nitric acid is manufactured from lower nitrogen oxides *via* an energy-consuming multi-step process.

In the presence of molecular oxygen (dioxygen) and an appropriate catalyst, nitrogen dioxide is activated to react with a wide variety of nonactivated and moderately activated aromatic substrates to afford the corresponding nitro compounds in good yield.[2] However, the isomeric composition of the nitration products obtained resembles in most cases those of classical nitration based on nitric and sulfuric acids. This means the formation of a large proportion of unwanted products, *i.e.*, inevitable loss of materials. Smith and coworkers have recently reported that halobenzenes can be nitrated with nitrogen dioxide and dioxygen in the presence of zeolite Hβ catalyst to give products of nitration, in which the *para*-nitro isomer predominates over the *ortho*-isomer (*ortho* : *para* = 0.10–0.24).[3] The *ortho* : *para*-isomer ratio of conventional nitration is usually in the range 0.6–0.8. We have also observed a significant improvement of the isomer product ratios in the zeolite-assisted double Kyodai-nitration of toluene and chlorobenzene.[4] In the present paper, we wish to report a remarkable example of zeolite catalysis in the *nonacid* aromatic nitration, where the interaction between a polar substituent and the acidic sites on the inorganic solid surface would considerably improve the regioselectivity of nitration and in certain cases it can even lead to the reversal of isomer ratio of nitration products.

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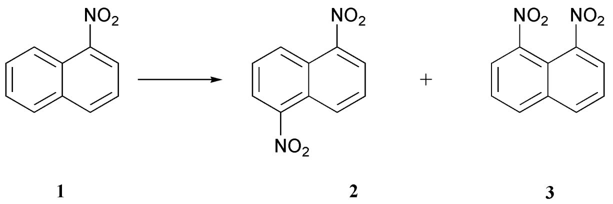
Results and discussion

Nitration of 1-nitronaphthalene

1,5-Dinitronaphthalene **2** and 1,8-dinitronaphthalene **3** are useful intermediates in the manufacture of dyestuffs, pigments, and high-energy materials. The former compound is also important as the precursor to high performance polyurethane resins and consequently of greater market demand than the latter. Industrial preparation of these polynitronaphthalenes still employs the traditional methodology involving a mixture of nitric and sulfuric acids, where the 1,5- : 1,8-dinitro isomer ratio of around 0.5–0.6 is always obtained either by direct nitration of naphthalene or by further nitration of 1-nitronaphthalene **1** (Table 1). The second nitro group preferentially occupies the position *peri* to the first nitro group irrespective of the nitrating conditions employed (Scheme 1).



Scheme 1

The Kyodai-nitration which uses a combination of lower nitrogen oxides and ozone as the nitrating agent has demonstrated excellent conversion of a wide variety of aromatic compounds into the corresponding nitro derivatives.[13] The non-acidic nature of this methodology is highly attractive and environmentally friendly. Unfortunately, when this nitrating system was applied to the nitration of compound **1**, the isomer proportion of the dinitration product was again similar to those of classical methodologies (Table 2, runs 1–3). No obvious improvement was observed in the presence of solid inorganic catalysts.

However, when compound **1** was subjected to the combined action of nitrogen dioxide and dioxygen in the presence of a

Table 1 Nitration of 1-nitronaphthalene with nitric acid alone or mixed acid

Entry	Nitrating agent	Reaction conditions	Yield (%)	Isomer proportion (%) 5-Nitro **2**	8-Nitro **3**	**2 : 3** ratio	Ref.
1	HNO_3 (*d* = 1.42)-H_2SO_4 (*d* = 1.84)	No solvent, 0 °C	—	31	69	0.45	5
2	HNO_3 (*d* = 1.42)-H_2SO_4 (*d* = 1.84)	No solvent, 0 °C	98.1	33.5	66.5	0.50	6
3	HNO_3 (*d* = 1.42)-H_2SO_4 (*d* = 1.84)	$(CH_3CO)_2O$, −40 °C	—	32.4	67.6	0.48	6
4	HNO_3 (*d* = 1.5)-H_2SO_4 (*d* = 1.84)	BF_3, CH_3CO_2H, 0 °C	98.3	33.3	66.7	0.50	6
5	HNO_3-H_2SO_4	No solvent, −55 °C	—	22	78	0.28	7
6	KNO_3-H_2SO_4 (*d* = 1.84)	No solvent, 0 °C, 24 h	—	36	64	0.56	8
7	HNO_3 (*d* = 1.42)	No solvent, reflux	—[a]	37.2	56.5	0.66	9
8[c]	53%-HNO_3-98%H_2SO_4	No solvent, 37–80 °C	93.7[b]	27.4	72.6	0.37	11
9[c]	NO_2-BF_3	CH_3NO_2. −5 °C	—	39	61	0.64	9
10[c]	fum-HNO_3-Claycop[d]	$(CH_3CO)_2O$–CCl_4, rt	93	25	75	0.33	12

[a] Accompanied by 1,3,8-trinitronaphthalene. [b] Accompanied by 1,4,5-trinitronaphthalene. [c] Direct dinitration of naphthalene. [d] Montmorillonite K10 impregnated with anhydrous cupric nitrate.

Table 2 Nitration of 1-nitronaphthalene with nitrogen dioxide and ozone or dioxygen in the presence of solid inorganic catalysts[a]

Run	Nitrating agent	Solvent	Catalyst[b]	Additive	Reaction time/h	Conversion[c] (%)	Yield[d] (%)	Isomer proportion (%)[e] 5-Nitro **2**	8-Nitro **3**	**2 : 3** Ratio
1	NO_2–O_3	CH_2Cl_2	—	—	2	>99	89	23	77	0.30
2	NO_2–O_3	CH_2Cl_2	HBEA-25	—	2	>99	89	25	75	0.33
3	NO_2–O_3	CH_2Cl_2	K10[f]	—	1	95	87	19	81	0.23
4	NO_2–O_2	CH_3CN	K10	—	7	100	90	26	74	0.35
5	NO_2–O_2[g]	CH_2Cl_2	—	—	48	51	17	45	55	0.82
6	NO_2–O_2[h]	CH_2Cl_2	—	—	48	74	27	38	62	0.61
7	NO_2–O_2[i]	CH_3CN	—	—	48	89	58	40	60	0.67
8	NO_2–O_2	CH_3CN	HZSM-5	—	7	35	21	52	48	1.08
9	NO_2–O_2	CH_3CN	HBEA-25	—	7	94	69	68	32	2.12
10	NO_2–O_2	CH_3CN	HBEA-25[j]	—	7	82	65	67	33	2.03
11	NO_2–O_2	CH_3CN	HBEA-25[k]	—	48	82	51	66	34	1.94
12	NO_2–O_2	CH_3CN	HBEA-25	CH_3SO_3H[l]	7	98	55	62	38	1.63
13	NO_2–O_2	CH_3CN	HBEA-25	$Fe(acac)_3$[m]	7	96	55	58	42	1.38
14	NO_2–O_2	CH_3CN	HBEA-25	H_2SO_4	7	>99	77	64	36	1.78
15	NO_2–O_2	CH_3CN	HBEA-25	$FeCl_3$[l]	7	>99	78	68	32	2.13
16	NO_2–O_2	CH_3CN	HBEA-150	—	7	99	85	72	28	2.57
17	NO_2–O_2	CH_3CN	FeBEA-150[n]	—	7	98	86	66	34	1.94
18	NO_2–O_2	CH_3CN	NaMFI-90	—	7	23	19	60	40	1.50
19	NO_2–O_2	CH_3CN	HSZ-390HOA	—	7	55	33	71	29	2.45
20	NO_2–O_2	CH_3CN	HSZ-690HOA	—	7	40	32	68	32	2.13

[a] All reactions with the NO_2–O_3 system were conducted at −10 °C using substrate **1** (9–10 mmol), liquid NO_2 (2.0 mL), catalyst (1.0 g), and CH_2Cl_2 (30 mL) under the Kyodai conditions, while those with the NO_2–O_2 system were carried out at room temperature using **1** (1.0 mmol), liquid NO_2 (0.5 ml) and catalyst (2.0 g) in CH_3CN (5 ml) under an oxygen almosphere, unless otherwise specified. [b] Zeolites and K10 clay were calcined at 500 and 300 °C, respectively, for 8 h in air prior to use. [c] Determined by GC. [d] Combined yield of **2** and **3** based on consumed **1**. [e] Calculated from GC peak areas, excluding other isomers and byproducts. [f] Double amount of catalyst was used. [g] Double amount of NO_2 was used. [h] Amount of NO_2 was increased to 2.0 mL. [i] Amount of substrate was increased to 2.9 mmol. [j] Amount of catalyst was decreased to 1.0 g. [k] Substrate (2.9 mmol) and catalyst (1.0 g) were used. [l] Around 20 mmol% amount to the substrate was added. [m] A 13 mmol% amount to the substrate was added. [n] Prepared by stirring a suspension of HBEA-150 (5 g) in 0.2 M aq. $FeCl_3$ solution (100 mL) for 24 h under reflux.

zeolite, the formation of **2** became highly favored, leading to the reversal of the 1,5- : 1,8-dinitro isomer ratios. Especially, in the presence of zeolite HBEA-150 or HSZ-390HOA, regioselection could be remarkably shifted towards the 1,5-dinitro isomer, the 1,5- : 1,8-dinitro isomer ratio reaching as high as 2.5–2.6 (runs 16 and 19). Polar solvent systems appeared to play a positive role in attaining a higher 1,5- : 1,8-dinitro isomer ratio. Both Brϕnsted and Lewis acids proved to be effective in the enhancement of reaction rate (runs 12–15). The H-type β-zeolite was superior to the Fe^{3+}-exchanged one in regioselection, probably due to the high density of effective sites that could interact *via* the hydrogen bonding (runs 16 and 17). Zeolite HBEA-150 with a high Si : Al ratio showed a better 1,5-site selectivity than HBEA-25 with a lower ratio possibly due to the dealuminiation, which would modify the distribution of the size and shape of the pores in the zeolites. Y-type zeolite HSZ-390HOA with three-dimensional channels of a large pore size exhibited high regioselectivity, probably due to its structural similarity to HBEA-150. Mordenite zeolite HSZ-690HOA with a linear array of large pores showed high regioselection but low conversion. Both selectivity and conversion were unsatisfactory with zeolites HZSM-5 and NaMFI-90 (runs 8 and 18). This may be attributed to the medium pore size structure, which would place more restriction on the transport of a substrate through the pores.

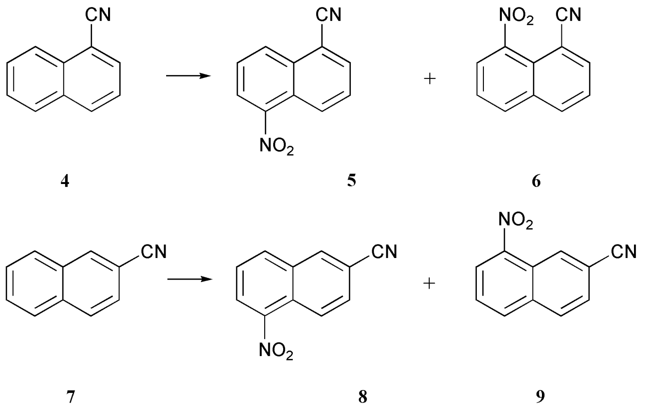
Montmorillonite K10 facilitated the reaction and gave a cleaner nitration product as compared with others. Unfortunately, the isomer ratio was not much different from those of classical nitration reactions. Air could be used as a partner of nitrogen dioxide, although oxygen shortened the reaction time much more. Recovered zeolites can be recycled without any appreciable loss of catalytic activity. It is most likely that the electrostatic interaction as well as the hydrogen bonding between the nitro group and the acidic sites forbid free mobility of **1** within the zeolite cages and render the *peri*-position of **1** less accessible toward NO_2^+ ions, thus leading to the reversal of the 1,5 : 1,8-dinitro isomer ratio.

A similar nonacid nitration of 2-nitronaphthalene was not investigated because of the strong mutagenic and carcinogenic nature of this compound.

Nitration of naphthonitriles, methylbenzonitriles (tolunitriles), and dimethylbenzonitriles (xylonitriles)

As an extension, we have investigated a similar nonacid nitration of another type of deactivated arene, aromatic nitriles, which included 1- and 2-naphthonitriles **4** and **7**, 2-, 3- and 4-methylbenzonitriles (*o*-, *m*- and *p*-tolunitriles) **10**, **13** and **17**, and three isomeric dimethylbenzonitriles (2,4-, 2,5- and 3,4-xylonitriles) **19**, **23** and **26**. Nitro derivatives of these nitriles are versatile starting materials for a variety of nitrogen-containing heterocyclic compounds of pharmaceutical and agrochemical interest. However, they are usually obtained not by direct nitration of nitriles but by the dehydration of nitroamides and nitroaldoximes,[14] treatment of diazotized nitroamines with CuCN[15] and prolonged heating of halonitriles with CuCN in DMF.[16] This could be due to the inconvenient separation of isomers which often form in comparable amounts as well as the susceptibility of the nitrile function toward strong protonic acids, especially at elevated temperatures.

Nitration of 1- and 2-naphthonitriles. Both 1- and 2-naphthonitriles **4** and **7** underwent a rapid Kyodai-nitration to give a mixture of 5-nitro and 8-nitro derivatives **5**–**6** and **8**–**9** in almost quantitative combined yield (Scheme 2). In contrast to 1-nitronaphthalene **1**, the 5-nitro isomers **5** and **8** were always favoured over the corresponding 8-nitro isomers **6** and **9**, the 5-nitro : 8-nitro isomer ratios being 1.27 and 1.33, respectively. The values are close to those (1.44 and 1.38, respectively) observed in the conventional nitration based on nitric and sulfuric acids (Table 3). Nitrile **4** was previously nitrated with nitronium tetrafluoroborate[17] and fuming nitric acid.[18] However, no information was available on the isomer composition of the products.



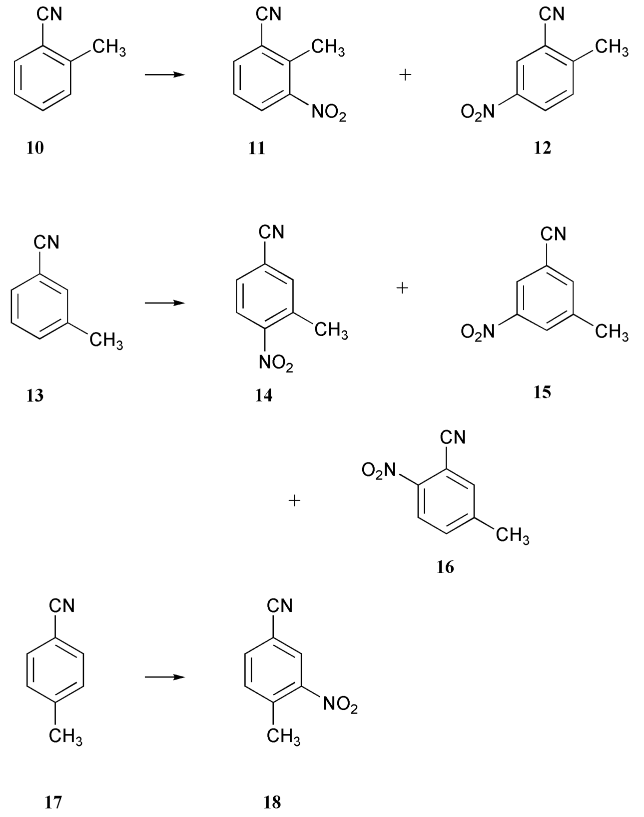
Scheme 2

The nitriles **4** and **7** were quite slow to react with nitrogen dioxide and dioxygen at room temperature to form a comparable amount of 5-nitro : 8-nitro isomers. The ratios of both isomers **5** : **6** and **8** : **9** fell in the range 1.1–1.2, the 5-nitro isomer being a little favoured over the 8-nitro isomer. In the presence of zeolites, however, the reaction became considerably facilitated and within 12 h it was almost complete. Rather surprisingly, the 5-nitro isomer **5** was remarkably favoured at the expense of the 8-nitro isomer **6** in the nitration of 1-naphthonitrile **4**, the 5-nitro : 8-nitro ratio reaching as high as 9.0 (Table 3). In contrast, the 8-nitro isomer **9** became more important in the similar reaction of 2-naphthonitrile **7** and the 5-nitro : 8-nitro ratio **8** : **9** was reversed from near the unity down to 0.72.

The isomer ratios were considerably dependent on the type of zeolites employed. The highest regioselection was attained with HBEA-150 for nitrile **4**, while the maximum reversal of isomer ratios was observed with HSZ-960HOA for nitrile **7**. A protonic acid such as methanesulfonic acid was also found to facilitate the nitration by nitrogen dioxide and dioxygen, but under these conditions the regioselection became worse, the 5-nitro : 8-nitro isomer ratios approaching unity.

Methylbenzonitriles (tolunitriles). As previously reported,[19] benzonitrile readily undergoes the Kyodai nitration to afford an isomeric mixture of nitrobenzonitriles (*ortho* : *meta* : *para* = 15–22 : 72–80 : 5–6) in high yield. However, benzonitrile was found to be almost inert toward the combined action of nitrogen dioxide and dioxygen at room temperature, little nitration products being obtained even after prolong contact in the presence of solid catalyst.

Three isomeric methylbenzonitriles **10**, **13** and **17** were also inert toward nitrogen dioxide and dioxygen under similar conditions. In the presence of zeolites, however, the reaction became considerably facilitated and satisfactory results were obtained after 24 h (Scheme 3). The most attractive feature of the present nitration methodology is the enhanced regioselectivity as compared with the traditional and the Kyodai-nitrations. The reaction proceeded slowly, but the product was simple and clean with little formation of higher nitration products.



Scheme 3

2-Methylbenzonitrile (*o*-tolunitrile) **10** reacted with nitric and sulfuric acids to give a mixture of 3-nitro and 5-nitro isomers **11** and **12** in a ratio of 37 : 63 (Table 4). The Kyodai nitration of nitrile **10** readily took place at lower temperature and gave an isomeric mixture of a similar composition (39 : 61). When the nitrile was reacted with nitrogen dioxide and dioxygen in the presence of zeolite, the regioselectivity was remarkably improved and the 5-nitro isomer became the predominant product. Especially, in the case of HBEA-25, the 5-nitro isomer was the exclusive product at 77% conversion level. HZS-960 and 980HOA were more effective in accelerating the reaction, but the regioselectivity was decreased.

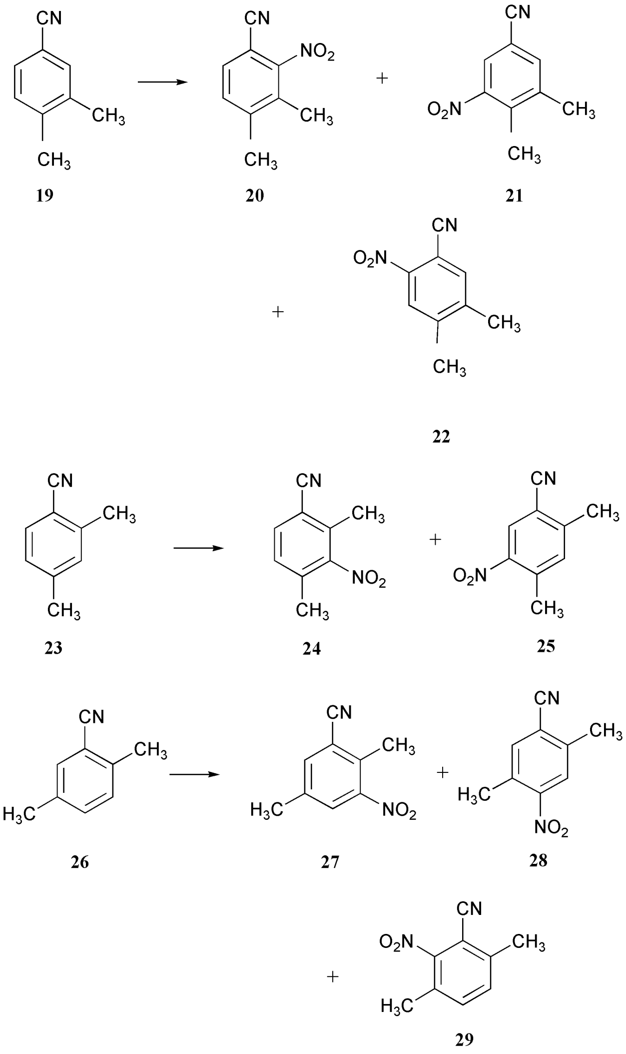
Table 3 Nitration of 1- and 2-naphthonitriles with nitrogen dioxide and ozone or dioxygen in the presence of zeolites[a]

Nitrile	Nitrating agent[a]	Catalyst	Temp./°C	Reaction time/h	Conversion (%)[b]	Isomer proportion (%)[b]		Isomer ratio
						5-nitro	8-nitro	
1-Naphthonitrile **4**						**5**	**6**	**5 : 6**
	NO_2–O_3[c]	—	−10	0.5	>99	56	44	1.27
	HNO_3 (d = 1.5)–H_2SO_4 (d = 1.84)	—	RT	8	>99	59	41	1.44
	NO_2–O_2	—	RT	24	56	54	46	1.17
	NO_2–O_2	CH_3SO_3H	RT	24	>99	50	50	1.00
	NO_2–O_2	HBEA-150	RT	12	>99	90	10	9.00
	NO_2–O_2	Hβ-25	RT	12	>99	86	14	6.14
	NO_2–O_2	HSZ-930HOA	RT	12	>99	73	27	2.70
	NO_2–O_2	HSZ-940HOA	RT	12	>99	69	31	2.23
	NO_2–O_2	HSZ-960HOA	RT	12	>99	84	16	5.25
	NO_2–O_2	HSZ-980HOA	RT	12	97	72	28	2.57
2-Naphthonitrile **7**						**8**	**9**	**8 : 9**
	NO_2–O_3[c]	—	−10	0.5	>99	57	43	1.33
	HNO_3 (d = 1.5)–H_2SO_4 (d = 1.84)	—	36	3	>99	58	42	1.38
	NO_2–O_2	HBEA-150	RT	12	>99	47	53	0.89
	NO_2–O_2	HSZ-930HOA	RT	12	>99	43	57	0.75
	NO_2–O_2	HSZ-940HOA	RT	12	>99	47	53	0.89
	NO_2–O_2	HSZ-960HOA	RT	12	>99	42	58	0.72
	NO_2–O_2	HSZ-980HOA	RT	12	>99	47	53	0.89

[a] All reactions were carried out in acetonitrile in the presence of an excess of NO_2, unless otherwise noted. For detail, see the Experimental Section. [b] Determined by GC. [c] Nitromethane was used as the solvent.

The traditional nitration of 3-methylbenzonitrile (*m*-tolunitrile) **13** at room temperature gave a mixture of 6-nitro, 5-nitro- and 4-nitro isomers **16**, **15** and **14** in a ratio of 40 : 6 : 54. Interestingly, the Kyodai-nitration of this nitrile gave an isomeric mixture of a different composition (14 : 63 : 23). The minor product **15** from the traditional nitration became most important in the Kyodai-nitration. When nitrile **13** was allowed to react with nitrogen dioxide and dioxygen in the presence of zeolites, the regioselectivity was remarkably improved, mainly leading to the 6-nitro isomer **16** at the expense of other two isomers **14** and **15**. A single recrystallization from ethanol of the crude nitration product gave the 6-nitro derivative, almost free from other isomeric impurities. HSZ-960HOA was most effective in accelerating the reaction and also exhibited better regioselection. 4-Methylbenzonitrile (*p*-tolunitrile) **17** gave the 3-nitro derivative **18** as a single product. In this case, HBEA-150 was found to be most effective in facilitating the reaction. Methylated benzonitriles were previously nitrated with fuming nitric acid alone or with sulfuric acid,[20] potassium nitrate–sulfuric acid,[21] acetyl nitrate,[3c] and nitronium tetrafluoroborate.[17] However, the literature contains no detail as to the isomer proportion of the nitration products.

Dimethylbenzonitriles (xylonitriles). Three isomeric dimethylbenzonitriles **19**, **23** and **26** were found to react more readily with nitrogen dioxide and dioxygen in the presence of zeolites, giving the corresponding nitro derivatives as an isomeric mixture (Scheme 4). In every case, the regioselectivity was remarkably improved as compared with both the traditional and Kyodai nitrations. Noteworthy is the nitration of nitrile **19**, where the 6-nitro isomer **22** was obtained as the single product in the presence of HSZ-960–980HOA (Table 5). Both the traditional and Kyodai-nitration of nitrile **19** afforded three isomeric nitration products in comparable amounts. Such remarkable regioselection may be attributed to the increased acidity of active sites as well as the fitness of pore sizes in HSZ-960–980HOA, since the conversion became quite low with HSZ-930–940HOA.



Scheme 4

The traditional nitration of 2,4-dimethylbenzonitrile **23** usually produces 3- and 5-nitro isomers **24** and **25** in an approximate ratio of 2 :5. In the presence of HSZ-960HOA, the regioselectivity is remarkably improved in favour of the latter isomer. From a single recrystallization in ethanol, compound **25** was obtained in a high state of purity. Both the traditional and the Kyodai nitrations of nitrile **26** gave 3- and 6-nitro isomers **29** and **27** as the major products. Zeolite HSZ-930HOA was found

Table 4 Nitration of methylbenzonitriles with nitrogen dioxide and ozone or dioxygen in the presence of zeolites[a]

Nitrile	Nitrating agent[a]	Catalyst	Temp./°C	Reaction time/h	Conversion (%)[b]	Isomer proportion (%)[b]			Isomer ratio	
2-Methylbenzonitrile (*o*-tolunitrile) **10**						3-Nitro **11**	5-Nitro **12**		**12** : **11**	
	NO_2–O_3	—	−10	3	100[c]	39	61[c]		1.56	
	HNO_3 (*d* = 1.5)–H_2SO_4 (*d* = 1.84)	—	RT	24	76[c]	37	63[c]		1.70	
	HNO_3–$(CH_3CO)_2O$–TFAA	Hβ	−10	2	100	13	87		6.69[d]	
	NO_2	—	RT	24	0	—	—		—	
	NO_2–O_2	HBEA-25	RT	24	77	0	100		—	
	NO_2–O_2	HSZ-940HOA	RT	24	95	9	91		10.1	
	NO_2–O_2	HSZ-960HOA	RT	24	100	25	75		3.00	
	NO_2–O_2	HSZ-980HOA	RT	24	100	12	88		7.33	
3-Methylbenzonitrile (*m*-tolunitrile) **13**						4-Nitro **14**	5-Nitro **15**	6-Nitro **16**	**14** : **16**	**15** : **16**
	NO_2–O_3	—	−10	3	100[c]	14	63	23[c]	0.61	2.74
	HNO_3 (*d* = 1.5)–H_2SO_4 (*d* = 1.84)	—	RT	24	76[c]	40	6	54[c]	0.74	0.11
	NO_2	—	RT	24	0	—	—	—	—	—
	NO_2–O_2	HBEA-25	RT	24	23	8	Trace	92	0.09	—
	NO_2–O_2	HSZ-940HOA	RT	24	88	Trace	5	95	—	0.05
	NO_2–O_2	HSZ-960HOA	RT	24	100	Trace	6	94	—	0.06
	NO_2–O_2	HSZ-980HOA	RT	24	27	Trace	5	95	—	0.05
4-Methylbenzonitrile (*p*-tolunitrile) **17**						3-Nitro **18**				
	NO_2–O_3	—	−10	3	100[c]	~100				
	HNO_3 (*d* = 1.5)–H_2SO_4 (*d* = 1.84)	—	RT	24	86[c]	~100				
	NO_2	—	RT	24	0	—				
	NO_2–O_2	HBEA-150	RT	24	94	~100				
	NO_2–O_2	Hβ-25	RT	24	64	~100				
	NO_2–O_2	HSZ-960HOA	RT	24	46	~100				
	NO_2–O_2	HSZ-980HOA	RT	24	Trace	~100				

[a] See footnotes in Table 3. [b] See footnotes in Table 3. [c] Determined by ^{1}H-NMR. [d] Ref. 3c.

Table 5 Nitration of dimethylbenzonitriles with nitrogen dioxide and ozone or dioxygen in the presence of zeolites[a]

Nitrile	Nitrating agent[a]	Catalyst	Temp./°C	Reaction time/h	Conversion (%)[b]	Isomer proportion (%)[b]			Remark
3,4-Dimethylbenzonitrile (3,4-*o*-xylonitrile) **19**						2-Nitro **20**	5-Nitro **21**	6-Nitro **22**	
	NO_2–O_3	—	−10	1.5	89	31	49	20[c]	
	HNO_3 (d = 1.5)–H_2SO_1 (d = 1.84)	—	RT	15	100	33	45	22[c]	
	HNO_3–$(MeCO)_2O$	—	−10	24	41	14	28	9[d]	
	NO_2	—	RT	15	0	—	—	—	
	NO_2–O_2	HSZ-930HOA	RT	15	3	—	—	100[c]	
	NO_2–O_2	HSZ-940HOA	RT	15	8	—	17	83[c]	
	NO_2–O_2	HSZ-960HOA	RT	15	100	—	—	100[c]	
	NO_2–O_2	HSZ-980HOA	RT	15	100	—	—	100[c]	
2,4-Dimethylbenzonitrile (2,4-*m*-xylonitrile) **23**						3-Nitro **24**	5-Nitro **25**		Isomer ratio **25 : 24**
	NO_2–O_3	—	−10	1.5	100	26	74		2.84
	NO_2–O_3	—[e]	RT	1.5	100	18	82		4.56
	HNO_3 (d=1.5)/H_2SO_4 (d=1.84)	—	RT	15	100	30	70		2.33
	NO_2	—	RT	15	—	—	—		—
	NO_2–O_2	HSZ-930HOA	RT	15	95	4	96		24.0
	NO_2–O_2	HSZ-940HOA	RT	15	83	7	93		13.3
	NO_2–O_2	HSZ-960HOA	RT	15	99	3	97		24.3
	NO_2–O_2	HSZ-980HOA	RT	15	66	6	94		15.7
2,5-Dimethylbenzonitrile (2,5-*p*-xylonitrile) **26**						3-Nitro **27**	4-Nitro **28**	6-Nitro **29**	Dinitration products
	NO_2–O_3	—	−10	1.5	100	49	6	43	2
	NO_2–O_3	—[e]	−10	1.5	100	32	16	48	4
	HNO_3(d=1.5)–H_2SO_4 (d=1.84)	—	RT	15	100	34	7	59	0
	NO_2	—	RT	15	3	69	31	—	0
	NO_2–O_2	HSZ-930HOA	RT	15	96	17	39	44	0
	NO_2–O_2	HSZ-940HOA	RT	15	94	11	44	45	0
	NO_2–O_2	HSZ-960HOA	RT	15	83	29	27	44	0
	NO_2–O_2	HSZ-980HOA	RT	15	97	19	18	63	Trace

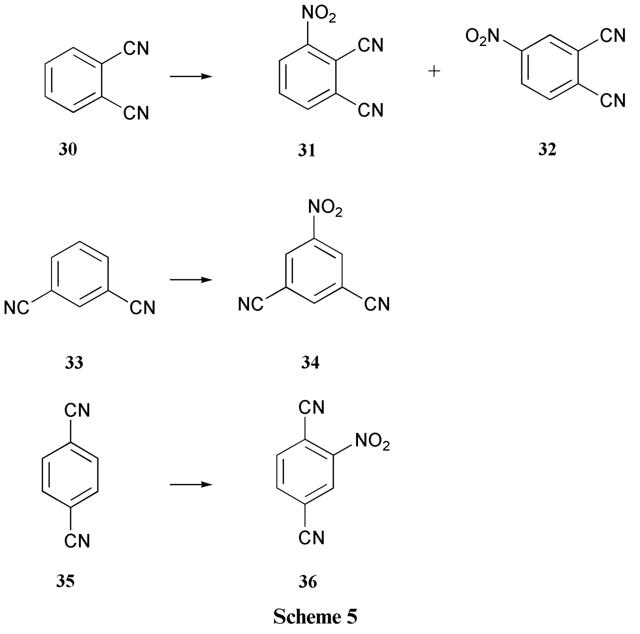
[a] See footnotes in Table 3. [b] Determined by ^{1}H-NMR. [c] Determined by GC. [d] Ref. 31, accompanied by 59% of addition products. [e] Dichloromethane was used as the solvent.

to favour the 4-nitro isomer **28** at the expense of the 6-nitro isomer **27**. The proportion of the 6-nitro isomer **29** was not much affected. In the presence of HSZ-960HOA, however, the isomer **27** became important at the expense of isomer **28**. In the absence of zeolites, compound **26** was quite slow to react. Interestingly, the 3-nitro isomer **27** became more important in this case and little or no 6-nitro isomer **29** was detected at this low conversion stage.

In the Kyodai-nitration of dimethylbenzonitriles, the product was always accompanied by small amounts of dinitration products. However, no such higher nitration products were observed in the zeolite-assisted nitration using nitrogen dioxide and dioxygen.

Kyodai-nitration of benzenendicarbonitriles

As expected, benzenedicarbonitriles were completely inert toward the combined action of nitrogen dioxide and dioxygen irrespective of the type of solid catalyst employed. However, with the intention of confirming the scope of the Kyodai-nitration, we have treated three isomeric benzenedicarbonitriles **30**, **33** and **35** with nitrogen dioxide in the presence of ozone. The reaction was quite slow and incomplete for all substrates even in the presence of a protonic acid or a Lewis acid as the catalyst, which included methanesulfonic acid, trifluoromethanesulfonic acid, and a variety of transition metal chlorides. However, a noticeable improvement was observed when a combination of protonic acid and metal chloride was employed as the catalyst. Thus, treatment of benzene-1,2-dicarbonitrile (phthalonitrile) **30** with nitrogen dioxide and ozone in the presence of methanesulfonic acid and iron(III) chloride at room temperature for 24 h gave a comparable mixture of 3- and 4-nitrobenzenene-1,2-dicarbonitrile **31** and **32** (Scheme 5). The conversion was not satisfactory, but the yield based on it was almost quantitative (Table 6). Dinitriles **31** and **32** are important as the starting material for a variety of phthalocyanines with peripheral substituents on the macrocyclic ring. However, they are usually prepared by a multi-step procedure starting from nitrophthalides.[22–24] Direct nitration of highly deactivated dinitrile **30** required heating with concentrated nitric and sulfuric acids at elevated temperatures, under which conditions the vicinal nitrile functions underwent extensive decomposition.



Scheme 5

5-Nitrobenzene-1,3-dicarbonitrile **34** is attractive as a starting material for iodine-based imaging agents. Thus, the Kyodai-nitration of benzene-1,3-dicarbonitrile (isophthalonitrile) **33** was investigated in some detail. Although a protonic acid or a metal halide alone proved to be ineffective as the catalyst, the combined use of methanesulfonic acid and iron(III) chloride was found to give an acceptable result. Compound **36** was obtained as the single product and the yield based on conversion was nearly quantitative. Under similar conditions, benzene-1,4-dicarbonitrile **35** gave 2-nitro derivative **36**. The ease of three isomeric benzenedicarbonitriles toward the Kyodai-nitration followed the order **33** > **30** > **35**. Dinitrile **35** was the least reactive of all and the attempted nitration of **35** by heating with nitric and sulfuric acids only led to an intractable tarry substance.

In summary, moderately deactivated arenes such as 1-nitronaphthalene, naphthonitriles, and methylated benzonitriles are nitrated with comparative ease by a combination of nitrogen dioxide and molecular oxygen in the presence of zeolite. The present results well demonstrate the great potential of zeolites in controlling the isomer proportion of nitration products, usually quite difficult or infeasible by traditional nitration methodologies, by modifying the framework topology and distribution of the size and shape of pores in zeolites.

Experimental

General

All reagents except compounds **7**, **19**, **23** and **26** were reagent-grade commercial products. The above four nitriles were prepared according to the reported procedure.[25] Montmorillonite K10 and zeolite HZSM-5 were purchased from Aldrich and Acros, respectively. Zeolites HBEA-25, 150 and NaMFI-90 were a gift from the Catalyst Society of Japan. Zeolites HSZ-930, 940, 960 and 980HOA were a gift from the Research Institute of TOSOH Corporation, Ltd. The SiO_2–Al_2O_3 ratios of these products were 27.0, 37.1, 110 and 480, respectively.[26] Acetonitrile and dichloromethane were distilled from CaH_2 before use and stored over 4 Å molecular sieves under argon. Nitrogen dioxide (99% pure) was purchased from Sumitomo Seika Co., Ltd. in a cylinder and used after transfer distillation. Melting points were determined on a Yanaco MP S 3 apparatus and are uncorrected. Gas–liquid chromatographic analyses were carried out with a Shimadzu GC-17A instrument fitted with an AOC-17 auto injector and FID detector, using a DB-5 capillary column (30 m × 0.247 mm id) and a 25 QC2 BPX5 (25 m × 0.25 mm id) capillary column. Temperature programmed heating between 50 °C and 250 °C was employed. The injection port and detector were at a temperature of 250 °C. Cyclododecane was used as an internal standard to evaluate the isomer composition and the identity of products was proven by direct comparison with authentic samples or by GC-MS analyses (Shimadzu GCMS-QP 5000 using isobutane as an ionizing gas). ^{1}H-NMR spectra were determined in $CDCl_3$ on a JEOL JNM-A-400 NMR spectrometer using tetramethylsilane as an internal standard. IR measurements were made on a JEOL FTIR-5300 spectrophotometer for KBr pellets and only characteristic peaks were recorded. Microanalyses were performed at the Advanced Instrumentation Center, Ehime University. All product yields presented in Tables 2–6 were not optimized.

Zeolite-assisted aromatic nitration using nitrogen dioxide and dioxygen

Nitration of nitronaphthalene and naphthonitriles. Typical procedure. 1-Naphthonitrile **4** (140 mg, 0.9 mmol), liquid NO_2 (0.5 mL, 15 mmol), zeolite (700 mg), and acetonitrile (20 mL) were placed in a flask. Oxygen was passed into the system to replace air, and a balloon filled with oxygen was connected. The mixture was stirred for 12 h at room temperature and progress of the reaction was monitored intermittently by TLC on a plastic sheet coated with silica gel 60 F_{254} (Merck). When the reaction was almost complete, excess NO_2 was expelled by blowing air into the solution and was collected in a cold trap for reuse.

Table 6 Catalyzed Kyodai-nitration of benzenedicarbonitriles[a]

Dinitrile	NO_2/mL	O_3/mmol	Catalyst	Conversion (%)[b]	Yield (%)[c]	
Benzene-1,2-dicarbonitrile (Phthalonitrile) **30**					3-Nitro **31**	4-Nitro **32**
	3.0	40	$CH_3SO_3H/FeCl_3$	35	50	50
Benzene-1,3-dicarbonitrile (isophthalonitrile) **33**					5-Nitro **34**	
	1.5	20	CH_3SO_3H	2	~100	
	1.5	20	$FeCl_3$	0	~100	
	1.5	20	$CH_3SO_3H–FeCl_3$	25	~100	
	1.5	20	$CF_3SO_3H–FeCl_3$	18	~100	
	1.5	20	$CF_3SO_3H–AICl_3$	12	~100	
	1.5	20	$CF_3SO_3H–ZnCl_2$	18	~100	
	1.5	20	$CF_3SO_3H–BlCl_3$	11	~100	
	3.0	40	$CH_3SO_3H–FeCl_3$	45	~100	
Benzene-1,4-dicarbonitrile (Terephthalonitrile) **35**					2-Nitro **36**	
	3.0	40	$CH_3SO_3H–FeCl_3$	23	~100	

[a] For detail, see the Experimental section. [b] Determined by ^{1}H-NMR. [c] Yield based on conversion.

The reaction mixture was evaporated under reduced pressure and the residue was extracted with ethyl acetate. The combined extracts were washed with brine, dried over $MgSO_4$, and evaporated to leave a solid residue, the composition of which was analyzed by GC and ^{1}H-NMR. For the isolation of each isomeric product, the residue was chromatographed on silica gel using hexane–EtOAc as the solvent to elute 5-nitro-1-naphthonitrile **5** and 8-nitro-1-naphthonitrile **6** in this order. A single crystallization of each fraction from ethanol gave **5** as light yellow crystals (58 mg, 32%) and **6** as red crystals (40 mg. 22%). The recovered zeolite was reused four times without appreciable loss of catalytic activity.

*5-Nitro-1-naphthonitrile (**5**).* Mp 205–207 °C (lit. 205[27] and 211–212 °C[14b]); ν_{max} (KBr)/cm^{-1} 2226 (CN), 1523 (NO_2), 1334 (NO_2), 794; δ_H ($CDCl_3$) 8.83 (d, 1H, J = 8.7), 8.59 (d, 1H, J = 8.1), 8.37 (dd, 1H, J = 7.8, 0.9), 8.09 (dd, 1H, J = 7.2, 0.9), 7.83 (t, 1H, J = 4.2), 7.79 (t, 1H, J = 7.2); m/z 198 (54), 152 (63), 140 (100), 125 (43).

*8-Nitro-1-naphthonitrile (**6**).* Mp 151–153 °C (lit.[14b] 153–154 °C); ν_{max}(KBr)/cm^{-1} 2226 (CN), 1523 (NO_2), 1536, 1338 (NO_2), 831, 756; δ_H ($CDCl_3$) 8.23 (dd, 1H, J = 8.4, 0.9), 8.16 (dd, 1H, J = 8.7, 1.5), 8.15 (dd 1H, J = 7.2, 1.5), 8.02 (dd 1H, J = 7.5, 1.2), 7.71 (m, 2H); m/z 198 (63), 168 (28), 152 (100), 140 (85), 125 (51).

*5-Nitro-2-naphthonitrile (**8**).* Mp 75–76 °C; (Found: C, 66.32; H, 2.96; N, 14.37. $C_{11}H_6N_2O_2$ requires C, 66.67; H, 3.05; N, 14.14%); ν_{max}(KBr)/cm^{-1} 2227 (CN), 1521 (NO_2), 1340 (NO_2), 802; δ_H ($CDCl_3$) 8.73 (d, 1H, J = 8.8), 8.42 (dd, 1H, J = 8.0, 1.2), 8.37 (d, 1H, J = 1.2), 8.21 (d, 1H, J = 8.4), 7.87 (dd, 1H, J = 9.2, 1.6), 7.73 (t, 1H, J = 8.0); m/z 198 (65), 168 (54), 152 (65), 140 (100), 125 (40).

*5-Nitro-2-naphthonitrile (**9**).* Mp 66–67 °C; (Found: C, 66.69; H, 3.20; N, 14.25. $C_{11}H_6N_2O_2$ requires C, 66.67; H, 3.05; N, 14.14%); ν_{max}(KBr)/cm^{-1} 2229 (CN), 1523 (NO_2), 1338 (NO_2), 842; δ_H ($CDCl_3$) 9.01 (s, 1H), 8.42 (dd, 1H, J = 8.0, 1.2), 8.21 (d, 1H, J = 8.4), 8.08 (d, 1H, J = 8.4), 7.77 (m, 2H); m/z 198 (78), 168 (25), 152 (95), 140 (100), 125 (58).

Nitration of methylated benzonitriles. General procedure. Methylbenzonitrile (30 mg, 0.3 mmol) or dimethylbenzonitrile (40 mg; 0.3 mmol), liquid NO_2 (0.5 mL, 15 mmmol), zeolite (400 mg), and acetonitrile (20 mL) were placed in a flask. Oxygen was passed into the flask to replace air and a balloon containing oxygen was connected. The mixture was magnetically stirred for a given time at room temperature, while progress of the reaction was intermittently monitored by TLC. When the reaction was almost complete, unchanged NO_2 was expelled by blowing air into the solution and was collected in a cold trap for reuse. The reaction mixture was evaporated under reduced pressure and the residue was extracted with ethyl acetate. The combined extracts were washed with brine, dried over $MgSO_4$, and evaporated. The product composition was analysed using GC and ^{1}H-NMR. For the isolation of each isomeric product, the residue was chromatographed on silica gel using hexane–EtOAc as the solvent.

*2-Methyl-3-nitrobenzonitrile (**11**).* Mp 68–69 °C (lit. 63–65[28a] and 69.5 °C[28b]); ν_{max}(KBr)/cm^{-1} 2234 (CN), 1532 (NO_2), 1352 (NO_2); δ_H ($CDCl_3$) 8.12 (dd, 1H, J = 1.2, 8.2), 7.87 (dd, 1H, J = 1.2, 8.0), 7.50 (t, 1H, J = 8.2), 2.79 (s, 3H); m/z 162 (17), 146 (10), 145 (100), 118 (10), 117 (61), 116 (22).

*2-Methyl-5-nitrobenzonitrile (**12**).* Mp 106–107 °C (lit.[29a] 104–106 °C); ν_{max}(KBr)/cm^{-1} 2236 (CN), 1524 (NO_2), 1352 (NO_2); δ_H ($CDCl_3$) 8.48 (d, 1H, J = 2.8), 8.34 (dd, 1H, J = 2.8, 8.6), 7.54 (dd, 1H, J = 0.8, 8.6), 2.69 (s, 3H); m/z 162 (100), 132 (34), 117 (29), 116 (96), 114 (17), 104 (28).

*3-Methyl-4-nitrobenzonitrile (**14**).* Mp 80–81 °C (lit.[29b] 80 °C); ν_{max}(KBr)/cm^{-1} 2236 (CN), 1524 (NO_2), 1350 (NO_2); δ_H ($CDCl_3$) 8.02 (d, 1H, J = 8.0), 7.67 (m, 2H), 2.63 (s, 3H); m/z 162 (13), 146 (11), 145 (100), 118 (10), 117 (53), 116 (23).

*3-Methyl-5-nitrobenzonitrile (**15**).* Mp 100–102 °C (lit.[16c] 104–105 °C); ν_{max}(KBr)/cm^{-1} 2240 (CN), 1534 (NO_2), 1360 (NO_2); δ_H ($CDCl_3$) 8.34 (s, 1H), 8.28 (s, 1H), 7.79 (s, 1H), 2.55 (s, 3H); m/z 162 (77), 131 (11), 126 (10), 117 (16), 116 (100), 104 (24).

*3-Methyl-6-nitrobenzonitrile (**16**).* Mp 92–93 °C (lit.[30] 93–94 °C); ν_{max}(KBr)/cm^{-1} 2236 (CN), 1524 (NO_2), 1350 (NO_2); δ_H ($CDCl_3$) 8.23 (d, 1H, J = 8.4), 7.70 (s, 1H), 7.59 (d, 1H, J = 8.4), 2.54 (s, 3H); m/z 162 (100), 132 (43), 116 (35), 104 (27).

*4-Methyl-3-nitrobenzonitrile (**18**).* Mp 106–107 °C (lit.[31] 107 °C); ν_{max}(KBr)/cm^{-1} 2234 (CN), 1526 (NO_2), 1352 (NO_2); δ_H ($CDCl_3$) 8.28 (d, 1H, J = 1.6), 7.87 (dd, 1H, J = 1.6, 7.8), 7.51 (d, 1H, J = 7.8), 2.69 (s, 3H); m/z 162 (21), 145 (100), 118 (15), 117 (57), 116 (22), 115 (10), 114 (11).

*3,4-Dimethylbenzonitrile (**19**).* Mp 67–68 °C (lit.[25] 65–66 °C); ν_{max}(KBr)/cm^{-1} 2224 (CN); δ_H ($CDCl_3$) 7.41 (s, 1H), 7.39 (d, 1H, J = 7.5), 7.21 (d, 1H, J = 7.5), 2.32 (s, 3H), 2.29 (s, 3H).

*3,4-Dimethyl-2-nitrobenzonitrile (**20**).* Mp 79–80 °C (lit.[32] 72–75 °C); ν_{max}(KBr)/cm^{-1} 2237 (CN), 1529 (NO_2), 1359 (NO_2); δ_H ($CDCl_3$) 7.42 (d, 1H, J = 8.8), 7.55 (d, 1H, J = 8.8), 2.44 (s, 3H), 2.30 (s, 3H).

*3,4-Dimethyl-5-nitrobenzonitrile (**21**).* Mp 119–120 °C (lit.[32] 116–118 °C); ν_{max}(KBr)/cm^{-1} 2241 (CN), 1529 (NO_2), 1367 (NO_2); δ_H ($CDCl_3$) 7.91 (s, 1H), 7.65 (s, 1H), 2.46 (s, 3H), 2.40 (s, 3H).

*3,4-Dimethyl-6-nitrobenzonitrile (**22**).* Mp 170–171 °C (lit.[33] 179–181 °C); ν_{max}(KBr)/cm^{-1} 2237 (CN), 1529 (NO_2), 1359

(NO_2); $\delta_H(CDCl_3)$ 8.11 (s, 1H), 7.64 (s, 1H), 2.45 (s, 3H), 2.42 (s, 3H).

*2,4-Dimethylbenzonitrile (**23**).* Oil.[25] ν_{max}(KBr)/cm^{-1} 2220 (CN); δ_H ($CDCl_3$) 7.48 (d, 1H, $J = 7.9$), 7.12 (s, 1H), 7.07 (d, 1H, $J = 7.9$), 2.50 (s, 3H), 2.37 (s, 3H).

*2,4-Dimethyl-3-nitrobenzonitrile (**24**).* Mp 122–123 °C; (Found: C, 61.32; H, 4.75; N, 15.92. $C_9H_8N_2O_2$ requires C, 61.36; H, 4.58; N, 15.90%); ν_{max}(KBr)/cm^{-1} 2230 (CN), 1527 (NO_2), 1373 (NO_2); $\delta_H(CDCl_3)$ 7.45 (d, 1H, $J = 7.9$), 7.41 (d, 1H, $J = 7.9$), 2.61 (s, 3H), 2.41 (s, 3H).

*2,4-Dimethyl-5-nitrobenzonitrile (**25**).* Mp 109–110 °C (lit.[21] 108 °C); ν_{max}(KBr)/cm^{-1} 2230 (CN), 1521 (NO_2), 1342 (NO_2); δ_H ($CDCl_3$) 7.87 (s, 1H), 7.60 (s, 1H), 2.60 (s, 3H), 2.57 (s, 3H).

*2,5-Dimethylbenzonitrile (**26**).* Oil.[25] ν_{max}(KBr)/cm^{-1} 2236 (CN), 1524 (NO_2), 1352 (NO_2); δ_H ($CDCl_3$) 7.39 (s, 1H), 7.28 (d, 1H, $J = 8.3$), 7.19 (d, 1H, $J = 8.3$), 2.49 (s, 3H), 2.33 (s, 3H).

*2,5-Dimethyl-6-nitrobenzonitrile (**27**).* Mp 76–77 °C (lit.[34a] 85 °C); ν_{max}(KBr)/cm^{-1} 2234 (CN), 1528 (NO_2), 1356 (NO_2); δ_H ($CDCl_3$) 7.45 (d, 1H, $J = 8.3$), 7.41 (d, 1H, $J = 8.3$), 2.60 (s, 3H), 2.41 (s, 3H).

*2,5-Dimethyl-4-nitrobenzonitrile (**28**).* Mp 117–118 °C;[34b] ν_{max}(KBr)/cm^{-1} 2235(CN), 1531 (NO_2), 1358 (NO_2); δ_H ($CDCl_3$) 7.87 (s, 1H), 7.60 (s, 1H), 2.60 (s, 3H), 2.57 (s, 3H).

*2,5-Dimethyl-3-nitrobenzonitrile (**29**).* Mp 117–118 °C (Found: C, 60.96; H, 4.89; N, 15.71. $C_9H_8N_2O_2$ requires C, 61.36; H, 4.58; N, 15.90%); ν_{max}(KBr)/cm^{-1} 2235 (CN), 1533 (NO_2), 1350 (NO_2); δ_H ($CDCl_3$) 7.92 (s, 1H,), 7.67 (s, 1H), 2.72 (s, 3H), 2.49 (s, 3H).

Kyodai-nitration of benzenedicarbonitriles. Typical procedure. Benzene-1,3-dicarbonitrile **33** (60 mg, 0.5 mmol), liquid NO_2 (3.0 mL, 90 mmol), methanesulfonic acid (52 mg), $FeCl_3$ (26 mg), and acetonitrile (30 mL) were placed in a two-necked flask fitted with an inlet tube and a vent which permits waste gas to escape. The mixture was cooled to −10 °C in an ice–salt bath, while a stream of ozonized oxygen was introduced under vigorous stirring through the gas inlet tube, which should dip just below the surface of the liquid in the flask. The progress of reaction was intermittently monitored by TLC. After 4 h, the cooling bath was removed, and the mixture was further stirred for 24 h at room temperature. Then, dry air was bubbled into the mixture to expel and recover unchanged nitrogen dioxide by cold trap. The mixture was evaporated under reduced pressure to leave a solid residue, which was extracted three times with dichloromethane. The combined extracts were washed with brine, dried, and evaporated. Chromatography of the resulting solid on silica gel using hexane–EtOAc as the solvent, followed by recrystallization from ethanol gave 5-nitrobenzene-1,3-dicarbonitrile **34** as colourless needles (35 mg, 41%). Unchanged dinitrile **33** was recovered in 55% yield.

*3-Nitrobenzene-1,2-dicarbonitrile (**31**).* Mp 165–166 °C (lit. 141[35] and 160 °C[22]); ν_{max}(KBr)/cm^{-1} 2240 (CN), 1541 (NO_2), 1354 (NO_2); δ_H ($CDCl_3$) 8.57 (dd, 1H, $J = 4.4$, 1.2), 8.15 (dd, 1H, $J = 8.0$, 0.8), 7.99 (t, 1H, $J = 8.4$); *m/z* 173 (84), 143 (84), 127 (68), 116 (49), 101 (51), 100 (100).

*4-Nitrobenzene-1,2-dicarbonitrile (**32**).* Mp 145–146 °C (lit.[23] 141 °C); ν_{max}(KBr)/cm^{-1} 2240 (CN), 1535 (NO_2), 1356 (NO_2); δ_H ($CDCl_3$) 8.69 (dd, 1H, $J = 0.4$, 2.0), 8.59 (dd, 1H, $J = 8.4$, 2.0), 8.07 (dd, 1H, $J = 0.4$, 8.4); *m/z* 173 (65), 127 (100), 101 (12).

*5-Nitrobenzene-1,3-dicarbonitrile (**34**).* Mp 214–215 °C (lit. 209–210[36a] and 204–205 °C[36b]); ν_{max}(KBr)/cm^{-1} 2245 (CN), 1543 (NO_2), 1385, 1354 (NO_2); δ_H ($CDCl_3$) 8.75 (d, 2H, $J = 1.5$), 8.27 (t, 1H, $J = 1.5$); *m/z* 173 (64), 128 (11), 127 (100), 101 (10), 100 (77).

*2-Nitrobenzene-1,4-dicarbonitrile (**36**).* Mp 124–125 °C (Found: C, 55.59; H, 2.16; N, 24.33. $C_9H_8N_2O_2$ requires C, 55.50; H, 1.75; N, 24.27%); ν_{max}(KBr)/cm^{-1} 2240 (CN), 1543 (NO_2), 1356 (NO_2); δ_H ($CDCl_3$) 8.63 (d, 1H, $J = 1.2$), 8.10 (m, 2H); *m/z* 173 (53), 127 (74), 100 (100).

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