Nonacid Nitration of Benzenedicarboxylic and Naphthalenecarboxylic Acid Esters

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When treated with nitrogen dioxide in the presence of ozone and a catalytic amount of iron(III) chloride in inert organic solvent at −10 to +5 °C, benzenedicarboxylic acid diesters **1**, **4**, and **6** underwent smooth nitration to give the corresponding mononitro derivatives **2**/**3**, **5**, and **7**, respectively, in good yield (kyodai nitration). Naphthalenecarboxylic acid esters **8** and **11** and naphthalene-1,8-dicarboxylic acid diester **16** were similarly nitrated in the absence of catalyst to give the expected nitro compounds **9**/**10**, **12**−**15**, and **17**−**22**, respectively. Different from conventional nitration based on the combined use of concentrated nitric and sulfuric acids, no hydrolytic cleavage of the ester function was observed under these conditions. The isomer distribution has been determined for the nitration of naphthalenecarboxylic acid esters **8**, **11**, and **16**, and spectral data were collected for less common nitro derivatives. A unique changeover of the orientation mode observed in the kyodai nitration of diester **16**, from the initial exclusive meta to the final meta/para, has been discussed in terms of the competition between the electrophilic substitution process involving the nitronium ion (NO_2^+) and the addition−elimination sequence involving the nitrogen trioxide radical ($^{\bullet}NO_3$).

Introduction

Nitro derivatives of benzenedicarboxylic acid diesters are important starting materials for a variety of fine chemical products including pharmaceuticals and agrochemical drugs. They are usually prepared by nitration followed by esterification of benzenedicarboxylic acids or by direct nitration of the corresponding diesters. Because of the poor miscibility of benzenedicarboxylic acids and their nitro derivatives with nitrating agent and/or organic solvent, the esters are generally preferred to free acids for synthetic purposes. Due to the combined electron-withdrawing effect of two ester functions, the aromatic ring is so deactivated that the nitration of diesters is usually carried out by heating gently with fuming nitric acid, preferably in concentrated sulfuric acid in which the substrates are protonated to go into solution. After the reaction, the mixture is diluted with water to collect the nitration product, which usually separates as a crystalline solid. This classical methodology is simple and easy to perform, but the major drawback is that it needs disposal of large amounts of acid drainage resulting from workup process. Additionally, the esters are in part hydrolyzed during the reaction and need a reesterification process to improve the quality and yield of the nitration products.

Previously, we have reported that nitrogen dioxide is activated in the presence of ozone to react readily with methyl benzoate under mild conditions to give the corresponding nitro derivatives in good yield (kyodai nitration).[1] As part of our continuing program to develop this new nitration methodology, we have herein extended it to isomeric benzenedicarboxylic acid diesters, i.e, phthalate, isophthalate, and terephthalate (**1**, **4** and **6**), and naphthalenecarboxylic acid esters, i.e., α- and β-naphthoic acid esters (**8** and **11**) and naphthalic acid ester (**16**).

Results and Discussion

On treatment with nitrogen dioxide in the presence of ozone, methyl benzoate readily underwent nitration to give an isomeric mixture of methyl nitrobenzoates in good yield.[2] The meta and ortho isomers were predominant (para/meta/ortho = 3:66:31) and relative importance of the latter isomer increased as compared to conventional nitration based on nitric acid and sulfuric acid (meta, 81−85%).[3] When attempts were made to extend this nonacid methodology to dimethyl benzenedicarboxylates, the results were unsatisfactory. The reaction was quite slow and incomplete even by the use of excess reagent. However, the addition of small amounts of a Lewis acid catalyst, especially iron(III) chloride, was found to facilitate the reaction remarkably and the expected nitro compounds were obtained in good yield (Scheme 1; Table 1). Of three isomeric dimethyl benzenedicarboxylates, isophthalate (**4a**) was most reactive, followed by tereph-

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(1) (a) For a survey of the kyodai nitration, see: Matsunaga, M. *Chimica Oggi* **1994**, 58−61. (b) Mori, T.; Suzuki, H. *Synlett* **1995**, 383−392. (c) Suzuki, T.; Noyori, R. *Chemtracts* **1997**, *10*, 813−817. (d) Ridd, J. H. *Acta Chem. Scand.* **1998**, *52*, 11−22. (e) Nonoyama, N.; Mori, T.; Suzuki, H. *Zh. Org. Khim.* **1998**, *34*, 1591−1601.

(2) Suzuki, H.; Tomaru, J.; Murashima, T. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2413−2416.

(3) Kamm, O.; Segur, J. B. *Organic Syntheses*; Wiley: New York, 1941; Collect. Vol. I, pp 372−374.

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Scheme 1

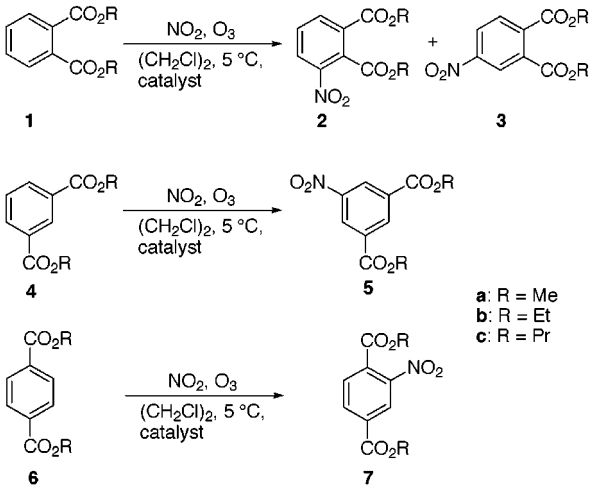


Table 1. Kyodai Nitration of Benzenedicarboxylic Acid Esters 1a,b, 4a,c, and 6a[a]

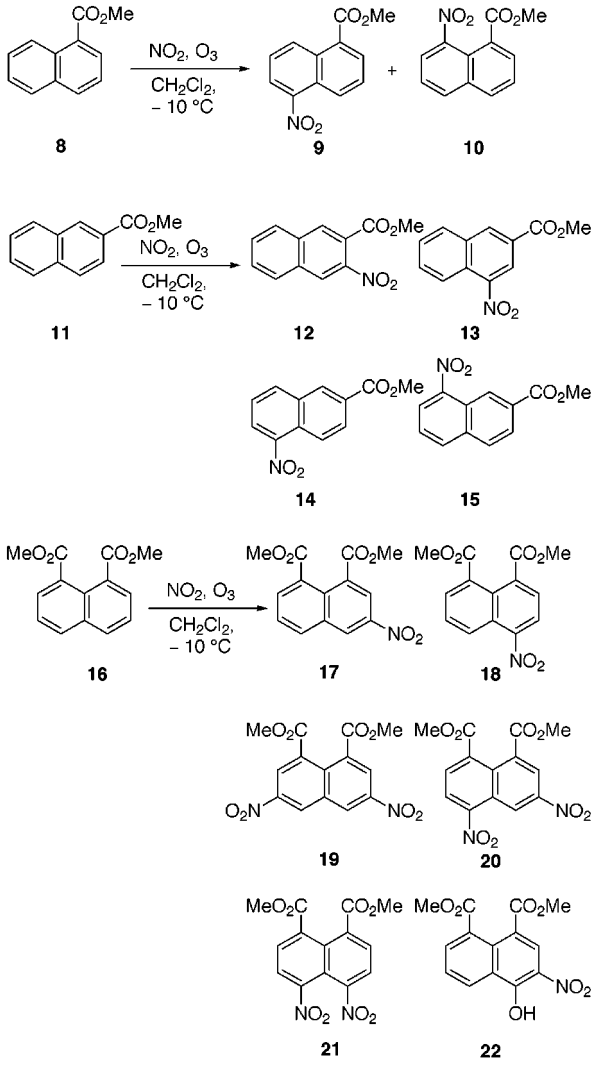
entry	substrate	NO_2 (equiv)	O_3 (equiv)	catalyst (mol %)	reaction time (h)	product yield (%)
1	**1a**[b]	3.3	3.0	$FeCl_3$, 2.2	3	**2a**, 52
						3a, 42
2	**1b**[b]	6.0	2.0	3.0	1.5	**2b**, 39
						3b, 38
3	**4a**	4.0	2.4	1.0	1.2	**5b**, 84
4		4.0	3.0	1.0	1.5	92
5		4.0	2.0	2.4	1.5	45[c]
6		4.0	2.0	PTA,[d] 50	1.5	87
7		4.0	2.0	$MeSO_3H$, 50	1.5	7
8		4.0	2.0	97% H_2SO_4, 50	1.5	10
9	**4c**	4.0	3.0	$FeCl_3$, 0.4	1.5	**5c**, 71
10		4.0	2.0	1.0	1.0	48
11		4.0	3.4	1.0	1.7	85
12		4.0	2.0	PTA,[d] 50	1.0	67
13		4.0	4.0	50	2.0	85
14	**6a**[b]	2.0	2.0	$FeCl_3$, 0.3	2.0	**7a**, 88
15		3.0	2.0	0.3	2.0	100

[a] All reactions were carried out using substrate (10 mmol), N_2O_4 (20−40 mmol) and O_3 (20−40 mmol) in 1,2-dichloroethane (30 mL) at 5 °C, unless otherwise noted. Yields refer to isolated compounds and were not optimized. [b] The solvent used was 25 mL. [c] Nitromethane was used as the solvent. [d] *p*-Toluenesulfonic acid monohydrate.

thalate (**6a**) and phthalate (**1a**), in that order. Protonic acids worked as catalyst also, but considerable amounts of acid catalyst were necessary to attain satisfactory conversion. Of the several protonic acids examined, *p*-toluenesulfonic acid proved to be the best. Methanesulfonic acid and sulfuric acid were not so effective. In a small-scale experiment, dichloromethane, acetonitrile, hexane, and nitromethane were the solvents of choice, but 1,2-dichloroethane was preferred in a preparative-scale experiment for reasons of low cost and lower volatility. Multiple nitration could not be observed even after prolonged reaction time.

Methyl naphthalene-1-carboxylate (**8**) readily reacted with nitrogen dioxide in the presence of ozone at −10 °C, giving the nitro derivatives **9** and **10** in good yield (Scheme 2; Table 2). Different from the above benzenedicarboxylates, no catalyst was necessary to attain satisfactory conversion. As expected, the nuclear substitution took place at unsubstituted ring, where the 8-nitro isomer (**10**) was formed in preference to the 5-isomer (**9**). The preferential attack at a position next to the electron-withdrawing substituent is in accordance with many

Scheme 2



precedents for the kyodai nitration.[4] In contrast, methyl naphthalene-2-carboxylate (**11**) underwent nitration at both substituted and unsubstituted rings (Scheme 2). Compared to the conventional nitration using mixed acid, the isomer **13** was favored at the expense of the isomer **15** in the kyodai nitration (Table 2; entry 2).

Naphthalene-1,8-dicarboxylic acid diester **16** underwent facile kyodai nitration under similar conditions to give a mixture of 3- and 4-nitro derivatives **17** and **18**, the former being predominant. As the reaction approached near 80% conversion, the second nitration began to start in the opposite ring, leading to three isomeric dinitro derivatives **19**−**21** and a phenolic product **22**. Almost similar ease in nitration observed for naphthalenemonocarboxylates **8** and **11** and naphthalenedicarboxylate **16** under the present conditions may be attributed to the diminished electron-withdrawing nature of the ester function in **16** due to the steric repulsion between two ester groups at the peri position, which thwarts the ester carbonyl function from coplanarity with the naphthalene ring.

In the kyodai nitration of diester **16**, the 3-nitro isomer **17** was formed as the only major substitution product at

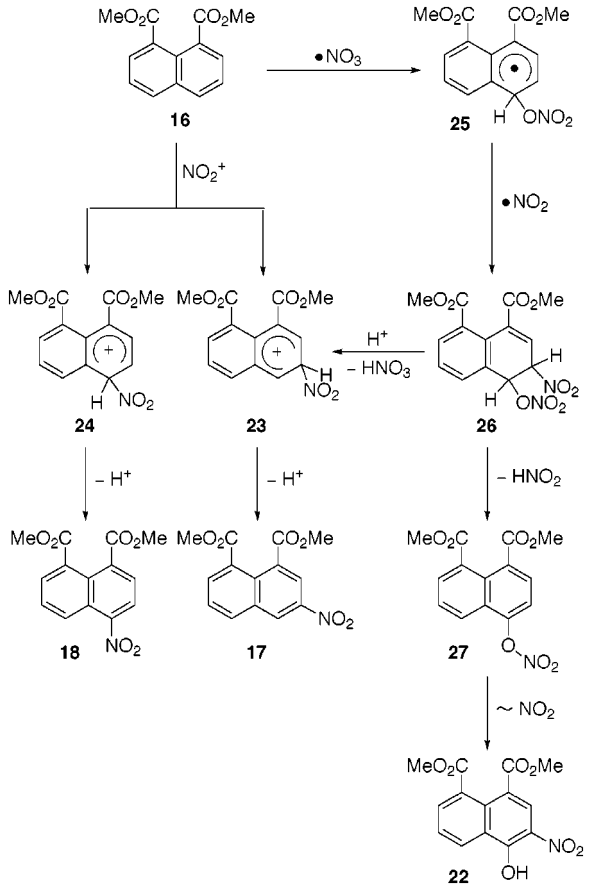
(4) (a) Suzuki, H.; Murashima, T.; Tatsumi, A.; Kozai, I. *Chem. Lett.* **1993**, 1421−1424. (b) Suzuki, H.; Murashima, T. *J. Chem. Soc., Perkin Trans. 1* **1994**, 903−908. (c) Suzuki, H.; Takeuchi, T.; Mori, T. *J. Org. Chem.* **1996**, *61*, 5944−5947.

Table 2. Nitration of Naphthalenecarboxylic Acid Esters 8 and 11[a]

						product composition[c] (%)					
entry	substrate	reagent	reaction time (min)	T (°C)	yield[b] (%)	**9**	**10**	**12**	**13**	**14**	**15**
1	**8**	NO_2-O_3	60	−10	76	23	77				
2	**11**	NO_2-O_3	50	−10	80			4	20	43	33
3		HNO_3 (1 equiv)−H_2SO_4	20	rt	84			3	14	45	38

[a] All reactions were performed using substrate (5 mmol), N_2O_4 (30 mmol), O_3 (10 mmol/h), and dichloromethane (30 mL). [b] Yields refer to isolated nitration products and were not optimized. [c] Determined by GC analysis.

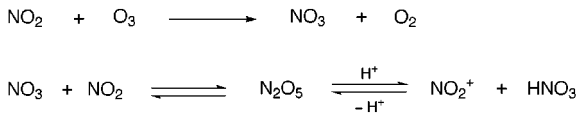
Scheme 3



the initial stage, accompanied by small amounts of a phenolic product **22**. As the reaction approached near 50% conversion, the 4-nitro isomer **18** began to appear and became increasingly important as the reaction proceeded. This interesting observation may be interpreted as follows: nitrogen dioxide ($^{\bullet}NO_2$) reacts with ozone (O_3) to generate nitrogen trioxide ($^{\bullet}NO_3$) as an electron-deficient neutral radical species, which adds to the naphthalene ring to form a radical intermediate **25** and subsequently trapped by nitrogen dioxide present in large excess to give an adduct **26** as the sole initial product (Scheme 3). Expulsion of nitrous acid from **26** leads to a nitrate ester **27**, which readily undergoes migration of the nitro group to give a phenolic product **22** via intramolecular nitration. The formation of phenolic byproducts during nitration has many precedents in the literature.[5] Protonation of adduct **26** by adventitious proton source will result in the formation of an arenium ion **23**, eventually leading to the 3-nitro isomer **17**.

(5) (a) Suzuki, H.; Mori, T. *J. Chem. Soc., Perkin Trans. 2* **1995**, 41−44. (b) Suzuki, H.; Mori, T. *J. Chem. Soc., Perkin Trans. 2* **1996**, 677−683. Also see: (c) Suzuki, H. *Synthesis* **1977**, 217−238. (d) Schofield, K. *Aromatic Nitration*; Cambridge University Press: London, 1980.

Scheme 4



Initially, this addition−elimination sequence would be predominant, but as the reaction goes further, the reaction system will gradually become acidic due to the accumulation of nitric acid arising from the decomposition of **26** to **23**. Under these conditions, the heterolytic cleavage of dinitrogen pentaoxide (N_2O_5), another oxidation product from nitrogen dioxide, becomes facilitated to generate nitronium ion (Scheme 4), which adds to both 3- and 4-positions of diester **16** to give intermediate ions **23** and **24**, leading to the appearance of **18** as the increasingly important product. Thus, the kyodai nitration of diester **16** may reasonably be considered to proceed as the competition between two different electrophilic processes involving the nitronium ion (NO_2^+) and the nitrogen trioxide radical ($^{\bullet}NO_3$), respectively, both generated in situ from nitrogen dioxide and ozone according to Scheme 4.

Conventional nitration of diester **16** with mixed acid gave the nitro diesters **17** and **18** nearly in a 1:1 ratio (Table 3, entry 6). This result means that nitronium ion attacks both 3- and 4-positions of **16** with similar ease. Especially noteworthy is the nitration of **16** with dinitrogen pentaoxide, where the isomer ratio of mononitration product **18**/**17** was found to decrease with the progress of the reaction (Figure 1). At the initial stage, the 4-nitro isomer **18** was predominant (**18**/**17** = 2.3), but the 3-nitro isomer **17** became increasingly important as the reaction proceeded, eventually the ratio reaching the value near 1.0. This tendency is opposite to that observed for the kyodai nitration, where the 3-nitro isomer **17** was formed as the sole initial product. This intriguing phenomenon may be interpreted as follows: under neutral conditions, diester **16** would first combine with dinitrogen pentaoxide to form a π-complex **29**, which then collapses to the 4-nitro diester **18** via an ionic intermediate **30** (Scheme 5). As the reaction proceeds, however, the substrate **16** would increasingly be protonated by the resulting nitric acid to form **28**, in which the electron-withdrawing ability of the ester function is strengthened and consequently the attack by nitronium ion would become more favored at 3-position rather than 4-position. Thus, with the progress of the reaction, the route **16** to **28** to **23** to **17** becomes increasingly favored over the alternative one **16** to **29** to **30** to **18**, resulting in the gradual decrease of the ratio **18**/**17**. The final isomer ratio was close to the value observed for the nitration of **16** with nitric acid-sulfuric acid (Table 3, entry 6). A marked difference in the composition of the initial products between the kyodai nitration and the nitration with dinitrogen pentaoxide strongly suggests a possible role

Table 3. Nitration of Naphthalene-1,8-dicarboxylic Acid Diester 16[a]

						product composition[c] (%)					
entry	reagent	solvent	*T* (°C)	reaction time (min)	yield[b] (%)	**17**	**18**	**19**	**20**	**21**	**22**
1	NO_2-O_3	CH_2Cl_2	−10	60	66	73	9	7	2		9
2	NO_2-O_3	CCl_4	−10	30	68	72	12	2			12
3	NO_2-O_3	MeCN	−10	30	69	64	18	5	3		10
4	NO_2-O_3, $MeSO_3H$	CH_2Cl_2	−10	30	68	70	13	8			9
5	N_2O_5	CH_2Cl_2	−10	60	64	37	42	7	3	5	6
6	HNO_3 (1 equiv)$-H_2SO_4$	CH_2Cl_2	rt	30	84	47	46	3	2	2	
7	HNO_3 (excess)$-H_2SO_4$	CH_2Cl_2	rt	30	78	27	37	16	13	7	

[a] All reactions were performed using diester **16** (5 mmol), N_2O_4 (30 mmol), O_3 (10 mmol/h), and dichloromethane (30 mL). [b] Yields are calculated by assuming all products are mononitro derivatives. [c] Determined by GC analysis.

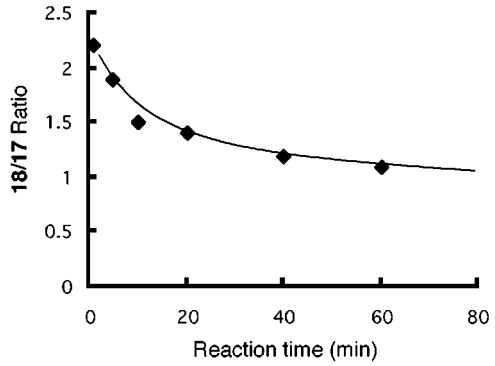
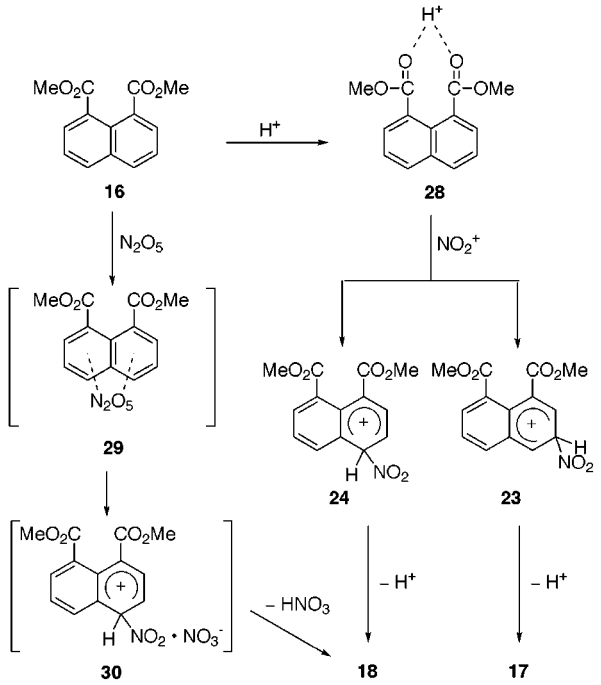


Figure 1. Time course variation of the **18/17** ratios in the nitration of diester **16** with N_2O_5. Reaction conditions: compound **16** (3 mmol), N_2O_5 (10 mmol), O_3 (10 mmol), CH_2Cl_2, −10 °C.

Scheme 5



of the nitrogen trioxide as the initial attacking species in the former reaction.

Experimental Section

Melting points were determined on a Yanagimoto hot-plate apparatus and are uncorrected. ^{1}H NMR spectra were recorded in $CDCl_3$ and/or DMSO-d_6 using TMS as an internal reference, unless otherwise mentioned. Coupling constants *J* are given in Hz. Infrared spectra were measured as KBr pellets or liquid films, and only prominent peaks were recorded. EI mass spectra were determined at 70 eV and CI mass spectra were obtained using isobutane as an ionizing gas. GC analyses were performed on a Shimadzu GC-14A gas chromatograph, using a CBP1-M25-025 column (25 m × 0.2 mm i.d.). Cyclododecane was used as an internal standard, except for the case of naphthalic acid diester **16**, where 1,3,5-trinitrobenzene was employed. Column chromatography was performed on silica gel (silica gel 60, Merck) using hexanes−ethyl acetate as the eluent. Elementary analyses were performed at the Microanalysis Laboratory, Institute of Chemical Research, Kyoto University.

Dichloromethane and 1,2-dichloroethane were distilled from CaH_2 prior to use. All substrate esters were obtained by boiling the corresponding carboxylic acids in an appropriate alcohol in the presence of an acid catalyst. Nitrogen dioxide (99% purity; impurities involve nitrogen monoxide and small amounts of nitrogen) was used from commercial cylinders, purchased from the Sumitomo Seika Co. Ltd. Dinitrogen pentaoxide was prepared by the literature procedure.[6] An apparatus (Nippon Ozone Co Ltd., type ON-1-2) was used for the generation of ozone at a rate of 10 mmol h^{-1}, with an oxygen flow of 10 dm^3 h^{-1} and an applied voltage of 80 V.

Kyodai Nitration of Benzenedicarboxylic Acid Esters 1, 4, and 6. Typical Procedure. A solution of methyl isophthalate **4a** (1.94 g; 10 mmol) in 1,2-dichloroethane (30 mL) was placed in a two-necked 50 mL flask fitted with a gas inlet tube and a vent and cooled to 5 °C by ice bath. Liquid nitrogen dioxide (3.0 g, 32 mmol) followed by iron(III) chloride (0.01 g) was quickly introduced with stirring, and a stream of ozonized oxygen was slowly passed through the gas inlet tube, submerged just below the surface of liquid. Throughout the reaction, ozonized oxygen was fed continuously at a low flow rate, and the progress of the reaction was monitored by TLC. After 1.5 h, the reaction was almost complete and excess nitrogen dioxide was expelled by blowing air into the solution and recovered in a cold trap for reuse. The reaction mixture was diluted with aqueous sodium hydrogen carbonate. The organic phase was separated, washed with water, dried ($MgSO_4$), and evaporated under reduced pressure to leave a crystalline solid, which was crystallized from methanol to give methyl 5-nitroisophthalate **5** (2.23 g, 86%), mp 123−125 °C (lit.[7] mp 123 °C).

Nitration of Naphthalenecarboxylic Acid Esters 8, 11, and 16. Typical Procedure. With Nitrogen Dioxide−Ozone. A solution of methyl naphthalene-1-carboxylate **8** (0.93 g; 5 mmol) in freshly distilled dichloromethane (30 mL) was placed in a two-necked 50 mL flask fitted with a gas inlet tube and a vent and cooled externally to −10 °C by an ethylene glycol bath. Liquid nitrogen dioxide (1.84 g; 20 mmol) was quickly introduced through a pipet, and then a stream of ozonized oxygen was slowly introduced through the gas inlet tube, submerged just below the surface of liquid. After 1 h, the reaction was almost complete and the mixture was diluted with aqueous sodium hydrogen carbonate. The organic phase was separated, washed with water, dried ($MgSO_4$), and

(6) Gruenhut, N. S.; Goldfrank, M.; Cushing, M. L.; Caesar, G. V. *Inorg. Synth.* **1950**, *3*, 78−81.
(7) *Dictionary of Organic Compounds*, 5th ed.; Chapman and Hall: London, 1988.

evaporated under reduced pressure to leave the crude product as an oily residue. The product was chromatographed on silica gel using hexanes−ethyl acetate (100:0−50:50) as the eluent to give nitro esters **9** and **10** both as light yellow crystalline solid.

With Fuming Nitric Acid and Concentrated Sulfuric Acid. To a stirred solution of naphthalene-1-carboxylic acid ester **8** (0.465 g; 2.5 mmol) in dry dichloromethane (30 mL) was added a mixture of fuming HNO_3 (0.7 g; 11 mmol) and concentrated H_2SO_4 (0.7 g) and the resulting mixture was stirred at room temperature. After 30 min the reaction was complete and the mixture was worked up as usual. The isomer ratio was estimated by ^{1}H NMR integration and the product was isolated by chromatography on silica gel using hexanes−ethyl acetate as eluent.

With Dinitrogen Pentaoxide. To a stirred solution of dinitrogen pentaoxide (1.1 g; 10 mmol) in dry dichloromethane (30 mL) cooled to −10 °C was added naphthalene-1-carboxylic acid ester **8** (0.23 g; 1.2 mmol), and the resulting mixture was stirred at this temperature for 80 min. At 10 min intervals, an aliquot was withdrawn and its composition was estimated by ^{1}H NMR integration.

All nitrobenzenedicarboxylic acid esters **2a**,**b**, **3a**,**b**, **5a**,**c**, and **7a** are known, and some are commercial products. Spectroscopic and analytical data for less common nitro compounds **9**, **10**, **12**−**15**, and **17**−**22** are shown below.

Methyl 5-nitronaphthalene-1-carboxylate (9): light yellow crystals; mp 107−108 °C (lit.[8] mp 107−109 °C); NMR δ_H ($CDCl_3$) 4.04 (3H, s, CH_3), 7.67−7.77 (2H, m), 8.21 (1H, d, J = = 7.6), 8.31 (1H, d, J = 7.6), 8.68 (1H, d, J = 9.2), 9.27 (1H, d, J = 9.2); IR ν_{max} (KBr)/cm^{-1} 1721 (C═O), 1516 (NO_2), 1339 (NO_2), 1277, 1154, 1059, 791, 768; MS m/z (CI) 232 (38, $M^+ + 1$), 202 (100).

Methyl 8-nitronaphthalene-1-carboxylate (10): light yellow crystals; mp 96.5−97.5 °C (lit.[8] mp 97−98 °C); NMR δ_H ($CDCl_3$) 3.90 (3H, s, CH_3), 7.61 (1H, t, J = 8.0), 7.67 (1H, dd, J = 7.2 8.0), 8.08 (1H, dd, J = 1.2 8.0), 8.11−8.16 (3H, m); IR ν_{max} (KBr)/cm^{-1} 1723 (C═O), 1524 (NO_2), 1343 (NO_2), 1277, 1209, 762; MS m/z (CI) 232 (62, $M^+ + 1$), 200 (100), 170 (88). Anal. Calcd for $C_{12}H_9NO_4$: C, 62.34; H, 3.92; N, 6.06. Found: C, 62.28; H, 3.94; N, 5.75.

Methyl 3-nitronaphthalene-2-carboxylate (12): colorless crystals; mp 195.5−196.5 °C; NMR δ_H ($CDCl_3$) 4.03 (3H, s, CH_3), 8.02 (2H, dd, J = 6.4, 8.4), 8.28 (1H, dd, J = 1.6 8.8), 8.36 (1H, dd, J = 1.6 8.8), 8.80 (1H, s), 8.92 (1H, d J = 1.2); IR ν_{max} (KBr)/cm^{-1} 1725 (C═O), 1528 (NO_2), 1346 (NO_2), 1279, 1233; MS m/z (CI) 232 (14, $M^+ + 1$), 202 (100), 113 (29).

Methyl 4-nitronaphthalene-2-carboxylate (13): light yellow crystals; mp 93−95 °C (lit.[9] mp 94−95 °C); NMR δ_H ($CDCl_3$) 4.04 (3H, s, CH_3), 7.72 (1H, t, J = 8.0), 7.85 (1H, t, J = 8.8), 8.10 (1H, d, J = 8.4), 8.59 (1H, d, J = 8.8), 8.80 (1H, d, J = 1.6), 8.86 (1H, s); IR ν_{max} (KBr)/cm^{-1} 1721 (C═O), 1528 (NO_2), 1298 (NO_2), 770; MS m/z (CI) 233 (14), 232 (100, $M^+ + 1$), 202 (23).

Methyl 5-nitronaphthalene-2-carboxylate (14): light yellow crystals; mp 109−110 °C (lit.[9] mp 112−112.5 °C); NMR δ_H ($CDCl_3$) 4.02 (3H, s, CH_3), 7.65 (1H, t, J = 8.0), 8.26 (1H, d, 8.0), 8.30 (1H, dd, J = 1.6 9.2), 8.36 (1H, dd, J = 1.2 8.0), 8.66 (1H, d, J = 9.6), 8.72 (1H, d, J = 1.2); IR ν_{max} (KBr)/cm^{-1} 1732 (C═O), 1522 (NO_2), 1327 (NO_2), 1298, 1265, 1208, 1107, 772; MS m/z (CI) 232 (8, $M^+ + 1$), 202 (100), 113 (15).

Methyl 8-nitronaphthalene-2-carboxylate (15): light yellow crystals; mp 131−132 °C;[10] NMR δ_H ($CDCl_3$) 4.02 (3H, s, CH_3), 7.68 (1H, t, J = 8.0), 8.03 (1H, d, J = 8.4), 8.18 (1H, d, J = 8.0), 8.24 (1H, dd, J = 1.6 8.8), 8.29 (1H, dd, J = 1.2 7.6), 9.29 (1H, s); IR ν_{max} (KBr)/cm^{-1} 1730 (C═O), 1522 (NO_2), 1342 (NO_2), 1283, 1190, 1109, 758; MS m/z (CI) 232 (30, $M^+ + 1$), 203 (19), 202 (100), 149 (35), 123 (23), 112 (43).

Dimethyl 3-nitronaphthalene-1,8-dicarboxylate (17): white needles; mp 146−148 °C (lit.[11] mp 145−146 °C); NMR δ_H ($CDCl_3$) 3.95 (3H, s, CH_3), 3.99 (3H, s, CH_3), 7.74 (1H, t, J = 8.0), 8.21 (2H, m), 8.75 (1H, d, J = 2.4), 8.94 (1H, d, J = 2.4); IR ν_{max} (KBr)/cm^{-1} 1728 (C═O), 1541 (NO_2), 1341 (NO_2), 1277, 1208; MS m/z (CI) 289 (19, $M^+ + 1$), 258 (23), 230 (25), 212 (33), 167 (39), 149 (100), 129 (27), 101 (59).

Dimethyl 4-nitronaphthalene-1,8-dicarboxylate (18): pale yellow needles; mp 126−127 °C (lit.[12] mp 125−126 °C); NMR δ_H ($CDCl_3$) 3.95 (3H, s, CH_3), 3.96 (3H, s, CH_3), 7.77 (1H, dd, J = 7.2 8.8), 8.06 (1H, d, J = 7.6), 8.12 (1H, d, J = 8.4), 8.15 (1H, dd, J = 1.2 6.8), 8.51 (1H, dd, J = 1.2 8.8); IR ν_{max} (KBr)/cm^{-1} 1723 (C═O), 1528 (NO_2), 1439, 1348 (NO_2), 1292, 1215, 1161, 1061, 1015, 866, 818, 766; MS m/z (CI) 289 (21, $M^+ + 1$), 258 (72), 230 (73), 212 (100), 184 (32), 169 (67), 149 (52), 126 (42), 113 (73).

Dimethyl 3,6-ninitronaphthalene-1,8-dicarboxylate (19): light yellow crystals; mp 202−204 °C; NMR δ_H ($CDCl_3$) 4.02 (6H, s, CH_3), 8.91 (2H, d, J = 2.0), 9.12 (2H, d, J = 2.4); IR ν_{max} (KBr)/cm^{-1} 1721 (C═O), 1618, 1530 (NO_2), 1337 (NO_2), 1267, 1024, 903; MS m/z (CI) 334 (37, $M^+ + 1$), 303 (100), 275 (61), 257 (88), 211 (33), 198 (38), 149 (78), 125 (33). Anal. Calcd for $C_{14}H_{10}N_2O_8$: C, 50.31; H, 3.02; N, 8.38. Found: C, 50.58; H, 3.22; N, 7.82.

Dimethyl 3,5-dinitronaphthalene-1,8-dicarboxylate (20): light yellow crystals; mp 189−191 °C; NMR δ_H ($CDCl_3$) 3.99 (3H, s, CH_3), 4.01 (3H, s, CH_3), 8.27 (1H, d, J = 8.0), 8.35 (1H, d, J = 8.4), 8.87 (1H, d, J = 2.4), 9.54 (1H, d, J = 2.0); IR ν_{max} (KBr)/cm^{-1} 1721 (C═O), 1537 (NO_2), 1439, 1348 (NO_2), 1285, 1208, 752; MS m/z (CI) 334 (29, $M^+ + 1$), 303 (65), 275 (100), 257 (40), 211 (62), 198 (24), 184 (25), 168 (34), 140 (20), 113 (27). Anal. Calcd for $C_{14}H_{10}N_2O_8$: C, 50.31; H, 3.02; N, 8.38. Found: C, 50.06; H, 3.14; N, 8.36.

Dimethyl 4,5-dinitronaphthalene-1,8-dicarboxylate (21): light yellow crystals; mp 243−245 °C (lit.[12] mp 247−249 °C); NMR δ_H ($CDCl_3$) 3.98 (6H, s, CH_3), 8.20 (2H, d, J = 8.0), 8.32 (2H, d, J = 8.0); IR ν_{max} (KBr)/cm^{-1} 1721 (C═O), 1543 (NO_2), 1437, 1354 (NO_2), 1287, 1206, 1044, 849, 725, 664, 511; MS m/z (CI) 334 (5, $M^+ + 1$), 288 (71), 260 (61), 230 (100), 199 (41), 184 (61), 169 (32), 156 (41), 149 (29), 141 (37), 115 (44), 113 (50).

Dimethyl 4-hydroxy-3-nitronaphthalene-1,8-dicarboxylate (22): yellow crystals; mp 131−133 °C; NMR δ_H ($CDCl_3$) 3.92 (3H, s, CH_3), 3.94 (3H, s, CH_3), 7.72 (1H, dd, J = 7.2 8.0), 8.21 (1H, dd, J = 1.2 7.2), 8.63 (1H, s), 8.73 (1H, dd, J = 1.2 8.0), 12.40 (1H, s); IR ν_{max} (KBr)/cm^{-1} 1719 (C═O), 1545 (NO_2), 1443, 1306 (NO_2), 1256, 1019, 772, 748; MS m/z (CI) 305.5 (99, $M^+ + 1$), 274 (93), 258 (50), 230 (59), 228 (60), 185 (100), 169 (49), 149 (67), 129 (92), 127 (78), 125 (45), 115 (61), 113 (88). Anal. Calcd for $C_{14}H_{11}NO_7$: C, 55.09; H, 3.63; N, 4.59. Found: C, 55.33; H, 3.68; N, 4.55.

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