Synthesis and Characterization of Some Nitrobenzanthrones: Suspected New Mutagens in Atmospheric Environment

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Five mononitro-, three dinitro- and one trinitrobenzanthrones have been synthesized by the modified Ullmann cross-coupling reaction between nitro-substituted 1-iodonaphthalene and methyl 2-iodobenzoates, followed by the Friedel–Crafts ring closure of the resulting 2-(1-naphthyl)benzoic acid derivatives.

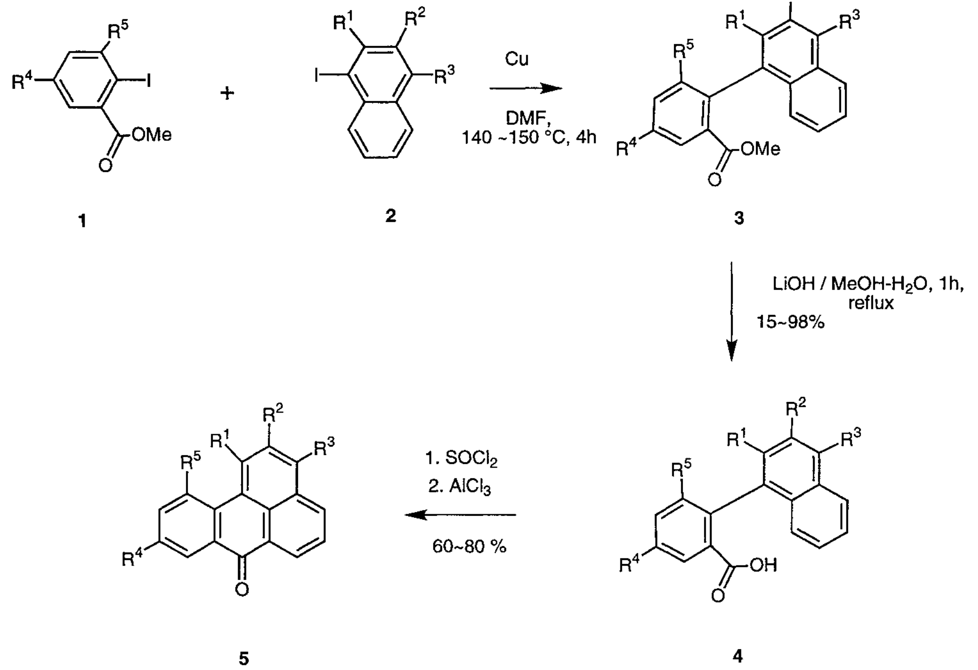
Polycondensed aromatic nitro compounds (nitro-PAHs) are known as universal contaminants in atmospheric environment. They exist in emission gas and particles from vehicle engines,[1,2] ambient air particulate matters,[3] coal fly ash, and smoke particles from burning woods,[4] and many of them have been found to be direct mutagens and/or carcinogens.[5] Especially, environmental occurrence and mutagenic activity of the nitro-PAHs such as nitropyrene, nitrofluoranthrene and nitrophenanthrene have been well established.[5,6] In atmospheric environment, however, there exist other types of suspected mutagens like oxy-PAHs and nitro-oxy-PAHs, but the identification and mutagenic study of those from environmental sources are often hampered by limited or difficult availability of known standard samples.

Recently, we have found that 3-nitrobenzanthrone (**5c**) is a new class of direct mutagen of atmospheric origin,[7] which shows the highest mutagenic activity in *Salmonella typhimurium* TA98 among the known mutagenic mononitro-PAHs from environmental source. Several isomeric mononitrobenzanthrones tested have revealed that they are less potent as mutagens than the 3-nitro isomer and that the 11-nitro isomer is devoid of mutagenicity (Table 1). Such a great dependence of mutagenic activity on the position of the nitro substituent has not so far been observed in the other series of nitro-PAHs. In order to get sight into the relationship between the structure and the mutagenic activity of isomeric nitrobenzanthrones, we have decided to synthesize some authentic mononitro-, dinitro- and trinitrobenzanthrones free from *isomeric impurities.*

Nitrobenzanthrones **5** can be obtained by direct nitration of benzanthrone with nitric acid in an organic solvent.[8,9] Major products are the 2-nitro- and 3-nitrobenzanthrones (**5b** and **5c**) and minor products include 1-nitro,

Table 1. Dependence of Direct-Acting Mutagenic Activity of Mononitrobenzanthrones **5c–e** on the Location of the Nitro Group

Compound	*Salmonella* Strain (revertants/*n* mol)	
	TA98	TA100
5c	208,400	29,790
5d	84,870	3,270
5e	6	6



Scheme

9-nitro, and 11-nitro isomers together with some higher nitration products such as 3,9-dinitro, 3,11-dinitro and 3,9,11-trinitro derivatives, which, however, are too difficult to be separated from one another by conventional laboratory methods so as to obtain the authentic samples free from isomeric contaminants. In an indirect approach, Craig and Woolhouse obtained the 11-nitro derivative **5e** using the Ullmann cross-coupling reaction between an iodonitrobenzene and an iodonaphthalenecarboxylic acid, followed by the Friedel-Crafts ring closure.[10] However, this approach is not free from possible contamination with the 9-nitro isomer, either.

We herein report an improved and well-defined procedure to obtain some nitrobenzanthrones **5** in good yield. The method involves the Ullmann cross coupling between nitro-substituted iodobenzoates **1** and iodonaphthalenes **2**, followed by the Friedel-Crafts ring closure of the resulting 2-(1-naphthyl)benzoic acids **4** via their corresponding acid chlorides as outlined in the Scheme.

In this synthetic route, the key step is the cross coupling between two substrates **1** and **2**. Although the Ullmann coupling reaction has been widely used as the convenient method for the aryl-aryl coupling, there are not so many successful reports of the cross coupling in the literature.[11] For example, Hawkins and Tucker carried out the Ullmann cross coupling of compounds **1e** and **4e** by a conventional procedure, but the yield of the expected cross coupling product was quite low.[12]

First, we performed the Ullmann coupling of compounds **1** and **2** according to the reported procedure,[12] and the results are summarized in Table 2. In runs 1, 3 and 6, the hetero coupling products were obtained in moderate yields; however in the other runs, we obtained mainly the homo coupling products and the hetero coupling products were mostly isolated in a yield below 20%. Especially, in runs 5 and 8, the yield of the hetero coupling products was only a trace amount.

In order to improve the yield of compound **4** in runs 4, 5 and 7-9, we modified the Ullmann method, i.e., methyl iodonitrobenzoate **1** dissolved in dimethylformamide (DMF) was added dropwise to a stirred mixture of compound **2**, copper bronze and DMF at a given temperature. The reaction temperature is crucial and must be carefully selected such that the homo coupling of compound **2** does not occur, i.e., for iodonaphthalene **2e** at 150 °C and for **2h** at 140 °C. Below or above these temperatures, the hetero coupling became less competitive and the homo coupling was predominant. At the optimum temperature, however, the hetero coupling reaction proceeded selectively, and compounds **3** were obtained in satisfactory yield for all runs 4, 5 and 7-9. Especially, for runs 5 and 8, the yields of the hetero coupling products were almost quantitative. This modified procedure was also applied to runs 1-3 and 6, but no improvement was observed. In run 3, the cross coupling between compounds **1c** and **2c** was so sluggish that a very slow addition of compound **1c** to the bulk of **2c** was necessary in order to avoid the homo coupling. In contrast, in runs 1 and 6, compounds **2a,f** were so reactive owing to the presence of the nitro substituent at the *ortho* position that it was quite difficult to optimize the reaction temperature at which the homo coupling of compounds **2a,f** did not proceed. In run 2, the reactivity of compound **2b** was considerably lowered owing to the adverse effect of the nitro group at the *meta* position, so that the yield of compound **3** could not be improved.

Demethylation of the hetero coupling products **3** was performed according to the reported method,[13] by heating with lithium hydroxide in methanol/water (9:1) under reflux for 1 hour. Under these conditions, compounds **4** were obtained almost quantitatively. At room temperature, the hydrolysis of esters **3** was quite slow partly because of their poor solubility in aqueous methanol. In a mixed solvent system like THF/methanol/water, a considerable amount of polymeric substance was formed and the separation of pure carboxylic acid **4** from tarry byproduct was tedious to effect.

Nitro-substituted 2-(1-naphthyl)benzoic acids **4** were made free from the accompanying small amounts of biphenyldicarboxylic acid by column chromatography on silica gel using acetonitrile as an eluent. When a highly pure specimen is needed, they can be further purified on ODS column using acetonitrile/water (6:4; pH 3) containing a small amount of H_3PO_4.

Carboxylic acids **4** were easily converted to their corresponding acid chlorides by thionyl chloride and the acid chlorides thus obtained were treated with 5 equivalents

Table 2. 2-(1-Naphthyl)benzoic Acid Derivatives **4a-i** Obtained by Ullmann Cross Coupling

Run		Product					Yield (%)[a]		Temperature[b]
		R^1	R^2	R^3	R^4	R^5	Method A	Method B	(°C)
1	**4a**	NO_2	H	H	H	H	62	34	150
2	**4b**	H	NO_2	H	H	H	15	16	180
3	**4c**	H	H	NO_2	H	H	50	48	150
4	**4d**	H	H	H	NO_2	H	20	96	150
5	**4e**	H	H	H	H	NO_2	trace	95	150
6	**4f**	NO_2	H	H	NO_2	H	64	35	150
7	**4g**	H	H	NO_2	NO_2	H	29	98	140
8	**4h**	H	H	NO_2	H	NO_2	trace	90	140
9	**4i**	H	H	NO_2	NO_2	NO_2	23	90	140

[a] Yields of isolated products are based on methyl iodobenzoates **1**.
[b] Optimum temperature for Method B.

of anhydrous $AlCl_3$ in chloroform at room temperature. Ring closure occurred smoothly to give the corresponding nitrobenzanthrones **5** in about 60 ~ 80 % yields. With the use of less than 5 equivalents of $AlCl_3$, the reaction became quite slow. No ring closure was observed when $SnCl_4$ was used instead of $AlCl_3$. The use of nitrobenzene or dichloromethane as the solvent was not effective to produce nitrobenzanthrones except in the cases of **5a** and **5f**, considerable amounts of byproduct being formed in most cases. Interestingly enough, however, compounds **5a** and **5f** were successfully obtained only by the use of nitrobenzene as the solvent. This may be attributed to both deactivating and the steric repulsion effects of the nitro group at the 2-position of the naphthalene nucleus.

Melting points were determined on a Yanagimoto hot stage apparatus and are uncorrected. IR spectra were recorded on a Shimadzu FTIR DR 8000/8100 IR spectrophotometer and only prominent peaks in 2000–700 cm^{-1} region were recorded. ^1H NMR spectra were obtained with a Varian Gemini-200 (200 MHz) spectrometer in $CDCl_3$ with TMS as an internal standard, except for compound **4f** in DMSO-d_6. J values are given in Hz. Electron impact mass spectra were recorded on a Shimadzu GC-MS QP-2000A spectrometer at 70 eV and chemical ionization mass spectra (CI-MS) on a Shimadzu GC-MS QP-5000 with DI-50 using isobutane as the reacting gas. TLC was performed by using Merck precoated silica gel sheets 60F-254. Silica gel (Wakogel) of the size 100–200 mesh was used for column chromatography. Iodonitronaphthalenes were prepared according to the reported method from the corresponding iodonaphthylamines.[14] 1-Amino-4-nitronaphthalene, 1-amino-3-nitronaphthalene and 1-amino-2-nitronaphthalene were obtained by the literature methods.[15–17] Methyl iodonitrobenzoates were synthesized from the corresponding aminonitrotoluenes according to the reported method.[18] Methyl 6-iodo-3,5-dinitrobenzoate was obtained from 6-chloro-3,5-dinitrobenzoic acid.[19,20] Elementary analyses were performed at Microanalysis Laboratory, Institute of Chemical Research, Kyoto University and all products gave satisfactory analytical results.

Ullmann Cross Coupling Between Methyl Iodobenzoate 1 and Iodonaphthalene 2; General Procedure:

Method A: To a stirred mixture of iodonaphthalene **2** (1 mmol) and methyl iodobenzoate **1** (1 mmol) heated at 150 °C, was added copper bronze powder (200 mg) in 4 portions over 3 h. After cooling, the mixture was treated with concd aq NH_4OH and then diluted with H_2O. The organic phase was extracted with EtOAc (5 × 20 mL), dried (Na_2SO_4), and evaporated. The thick oily residue was passed through a silica gel column using hexane/EtOAc (5 : 1) as the eluent and the fractions containing the Ullmann coupling products were collected. Evaporation of the solvent left a mixture of ester products as an oil (200 mg), which was dissolved in a solution of LiOH (500 mg) in H_2O/MeOH (1 : 9; 50 mL) and heated under reflux for 1 h. After cooling, the solution was made acidic with concd HCl and the organic phase was extracted with $CHCl_3$ (3 × 30 mL). The combined extracts were dried (Na_2SO_4) and evaporated on a rotatory evaporator. The oily residue was chromatographed on a silica gel column using MeCN as the eluent to obtain the expected coupling product **4** as a yellow powder. Sometimes, carboxylic acid **4** separated as an oil, which was then redissolved in KOH and made acidic with concd HCl to afford the same acid as a solid.

Method B: To a mixture of iodonaphthalene **2** (4 mmol) and copper bronze powder (500 mg) kept at 140 or 150 °C, a solution of methyl iodobenzoate **1** (1 mmol) in DMF (5 mL) was added dropwise over 4 h. After the addition, the mixture was cooled and diluted with H_2O. Aq NH_4OH was added to dissolve the copper salt and the resulting mixture was worked up as described in Method A.

1-(2-Carboxyphenyl)-2-nitronaphthalene (**4a**): pale yellow powder; mp 193–194 °C.

IR (KBr): ν = 1686, 1523, 1509, 1350 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.2–7.3 (m, 2 H), 7.4–7.5 (m, 1 H), 7.5–7.7 (m, 3 H), 8.0 (dd, J = 8.1, 3.1, 2 H), 8.1 (d, J = 9.0, 1 H), 8.2 (dd, J = 7.6, 1.9, 1 H).

MS: m/z (%) = 247 ($M^+ - NO_2$, 100), 202 (23), 189 (22).

1-(2-Carboxyphenyl)-3-nitronaphthalene (**4b**): yellow powder; mp 193–194 °C.

IR (KBr): ν = 1682, 1525, 1502, 1350 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.3–7.7 (m, 6 H), 8.1–8.2 (m, 3 H), 8.8 (d, J = 2.0, 1 H).

MS: m/z (%) = 293 (M^+, 100), 202 (42), 201 (33), 200 (30), 189 (33).

1-(2-Carboxyphenyl)-4-nitronaphthalene (**4c**): yellow powder; mp 220–221 °C.

IR (KBr): ν = 1684, 1510, 1334, 1315 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.3–7.7 (m, 7 H), 8.2 (dd, J = 7.7, 1.3, 1 H), 8.3 (d, J = 7.7, 1 H), 8.6 (d, J = 8.7, 1 H).

MS: m/z (%) = 293 (M^+, 100), 217 (27), 201 ($M^+ - CO_2H{-}NO_2$, 38), 200 (50), 189 (60).

1-(2-Carboxy-4-nitrophenyl)naphthalene (**4d**): yellow powder; mp 194–195 °C.

IR (KBr): ν = 1705, 1541, 1390, 1313 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.3–7.6 (m, 6 H), 7.9 (d, J = 8.1, 2 H), 8.5 (dd, J = 3.9, 2.3, 1 H), 8.9 (d, J = 2.3, 1 H).

MS: m/z (%) = 293 (M^+, 100), 202 (34), 201 ($M^+ - CO_2H{-}NO_2$, 25), 189 (22).

1-(2-Carboxy-6-nitrophenyl)naphthalene (**4e**): yellow powder; mp 174–175 °C.

IR (KBr): ν = 1684, 1529, 1508, 1360, 1307 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.2–7.5 (m, 5 H), 7.7 (t, J = 8.0, 1 H), 7.9 (d, J = 8.1, 2 H), 8.1 (dd, J = 8.1, 1.3, 1 H), 8.9 (dd, J = 7.9, 1.3, 1 H).

MS: m/z (%) = 293 (M^+, 100), 248 (40), 202 (60), 201 ($M^+ - CO_2H{-}NO_2$, 54), 189 (37).

1-(2-Carboxy-4-nitrophenyl)-2-nitronaphthalene (**4f**): light yellow powder; mp 247–248 °C.

IR (KBr): ν = 1697, 1522, 1336 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 7.2 (d, J = 8.4, 1 H), 7.5–7.8 (m, 3 H), 8.1–8.3 (m, 3 H), 8.5 (dd, J = 8.4, 2.4, 1 H), 8.8 (d, J = 2.4, 1 H).

CI-MS: m/z (%) = 339 ($M^+ + 1$, 100), 292 (57).

1-(2-Carboxy-4-nitrophenyl)-4-nitronaphthalene (**4g**): light yellow powder; mp 234–235 °C.

IR (KBr): ν = 1716, 1523, 1340 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.3–7.8 (m, 5 H), 8.3 (d, J = 7.3, 1 H), 8.5–8.7 (m, 2 H), 9.0 (d, J = 2.3, 1 H).

MS: m/z (%) = 338 ($M^+ - NO_2$, 93), 218 (29), 200 (48), 189 (100).

1-(2-Carboxy-6-nitrophenyl)-4-nitronaphthalene (**4h**): yellow powder; mp 227–228 °C.

IR (KBr): ν = 1699, 1537, 1512, 1329 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.3–7.6 (m, 3 H), 7.7–7.8 (m, 2 H), 8.1–8.2 (m, 2 H), 8.4 (dd, J = 7.8, 1.1, 1 H), 8.6 (d, J = 8.5, 1 H).

MS: m/z (%) = 338 ($M^+ - NO_2$, 100), 293 (36), 200 (64), 189 (83).

1-(2-Carboxy-4,6-dinitrophenyl)-4-nitronaphthalene (**4i**): yellow powder; mp 187–188 °C.

IR (KBr): ν = 1716, 1539, 1344 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.3–7.4 (m, 2 H), 7.6 (dt, J = 7.1, 1.3, 1 H), 7.8 (dt, J = 8.0, 1.3, 1 H), 8.2 (d, J = 8.0, 1 H), 8.5–8.6 (m, 1 H), 9.0 (d, J = 2.3, 1 H), 9.1 (d, J = 2.3, 1 H).

MS: m/z (%) = 338 ($M^+ - NO_2$, 13), 189 (100).

Ring Closure of Compounds 4a–i to Nitrobenzanthrones 5a–i; General Procedure:

Carboxylic acid **4** (1.5 mmol) was converted with excess $SOCl_2$ (30 mL) to the corresponding acid chloride, which was dissolved in $CHCl_3$ (50 mL) (in the case of **4a,f**, nitrobenzene was used as the solvent) and stirred with anhyd $AlCl_3$ (997 mg, 7.5 mmol) overnight at r.t. The reaction mixture was diluted with MeOH (10 mL) and treated with 1 M HCl. Organic layer was separated, dried (Na$_2$SO$_4$), and evaporated to obtain crude nitrobenzanthrone **5**, which was purified by chromatography on silica gel using hexane/CH$_2$Cl$_2$ as the eluent.

1-Nitro-7H-benz[d,e]anthracen-7-one (**5a**): pale yellow needles; mp 183–184 °C.

IR (KBr): ν = 1655, 1523, 1346, 1294 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 7.6–7.7 (m, 3 H), 7.8–7.9 (m, 2 H), 8.1 (d, J = 8.7, 1 H), 8.3 (dd, J = 8.2, 1.5, 1 H), 8.5–8.6 (m, 1 H), 8.8 (dd, J = 7.3, 1.3, 1 H).

MS: m/z (%) = 275 (M$^+$, 49), 245 (M$^+$ –NO, 100), 200 (83), 189 (72).

Anal. Calc. for C$_{17}$H$_9$NO$_3$: C 74.18; H 3.27; N 5.09. Found: C 74.51; H 3.26; N 5.09.

2-Nitro-7H-benz[d,e]anthracen-7-one (**5b**): yellow powder; mp > 300 °C (Lit.^{8} 305 °C).

IR (KBr): ν = 1664, 1527, 1348 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 7.7 (dt, J = 7.7, 1.1, 1 H), 7.9 (dt, J = 7.3, 1.6, 1 H), 8.0 (t, J = 8.1, 1 H), 8.4–8.6 (m, 3 H), 8.8–8.9 (m, 2 H), 9.2 (d, J = 2.1, 1 H).

MS: m/z (%) = 275 (M$^+$, 100), 245 (M$^+$ –NO, 40), 217 (21), 189 (11).

3-Nitro-7H-benz[d,e]anthracen-7-one (**5c**): yellow powder; mp 256–257 °C (Lit.^{9} 252 °C).

IR (KBr): ν = 1653, 1518, 1508, 1338 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 7.7 (dt, J = 7.3, 1.1, 1 H), 7.8 (dt, J = 7.6, 1.6, 1 H), 8.0 (dd, J = 8.7, 7.4, 1 H), 8.3–8.5 (m, 4 H), 8.9 (dd, J = 7.4, 1.2, 1 H), 9.0 (dd, J = 8.7, 1.2, 1 H).

MS: m/z (%) = 275 (M$^+$, 97), 245 (M$^+$ –NO, 100), 201 (51), 200 (77).

9-Nitro-7H-benz[d,e]anthracen-7-one (**5d**): yellow powder; mp 291–293 °C.

IR (KBr): ν = 1655, 1523, 1502, 1346 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 7.8–7.9 (m, 2 H), 8.2 (d, J = 8.3, 1 H), 8.3 (dd, J = 8.1, 1.3, 1 H), 8.5–8.6 (m, 3 H), 8.9 (dd, J = 7.3, 1.3, 1 H), 9.3 (s, 1 H).

MS: m/z (%) = 275 (M$^+$, 57), 245 (M$^+$ –NO, 100), 201 (26), 200 (35).

Anal. Calc. for C$_{17}$H$_9$NO$_3$: C 74.18; H 3.27; N 5.09. Found: C 73.93; H 3.30; N 5.04.

11-Nitro-7H-benz[d,e]anthracen-7-one (**5e**): yellow powder; mp 141–142 °C (Lit.^{10} 153–154 °C).

IR (KBr): ν = 1653, 1516, 1506, 1354 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 7.6–7.7 (m, 2 H), 7.8–7.9 (m, 2 H), 8.0–8.1 (m, 2 H), 8.3 (d, J = 8.5, 1 H), 8.7 (dd, J = 8.1, 1.3, 1 H), 8.8 (dd, J = 7.3, 1.3, 1 H).

MS: m/z (%) = 275 (M$^+$, 67), 245 (M$^+$ –NO, 93), 200 (82), 189 (100).

1,9-Dinitro-7H-benz[d,e]anthracen-7-one (**5f**): yellow powder; mp 273–274 °C.

IR (KBr): ν = 1662, 1522, 1506, 1346 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 7.8 (d, J = 8.7, 1 H), 7.9–8.1 (m, 2 H), 8.2 (d, J = 8.7, 1 H), 8.4 (dd, J = 8.5, 1.1, 1 H), 8.5 (dd, J = 8.5, 2.5, 1 H), 8.9 (dd, J = 6.7, 1.1, 1 H), 9.3 (d, J = 2.5, 1 H).

MS: m/z (%) = 320 (M$^+$, 62), 244 (100), 200 (68).

Anal. Calc. for C$_{17}$H$_8$N$_2$O$_5$: C 63.75; H 2.50; N 8.75. Found: C 63.67; H 2.44, N 8.63.

3,9-Dinitro-7H-benz[d,e]anthracen-7-one (**5g**): yellow powder; mp 277–278 °C.

IR (KBr): ν = 1662, 1522, 1506, 1346 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 8.1 (dd, J = 8.6, 7.3, 1 H), 8.4 (d, J = 8.3, 1 H), 8.5–8.7 (m, 3 H), 8.9–9.0 (m, 2 H), 9.4 (d, J = 2.2, 1 H).

MS: m/z (%) = 320 (M$^+$, 100), 200 (57).

Anal. Calc. for C$_{17}$H$_8$N$_2$O$_5$: C 63.75; H 2.50; N 8.75. Found: C 63.69; H 2.52; N 8.70.

3,11-Dinitro-7H-benz[d,e]anthracen-7-one (**5h**): yellow powder; mp 244–245 °C.

IR (KBr): ν = 1662, 1518, 1506, 1350 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 7.8 (t, J = 7.7, 1 H), 7.9–8.1 (m, 3 H), 8.3 (d, J = 8.4, 1 H), 8.7 (dd, J = 1.5 and 7.7, 1 H), 8.8 (dd, J = 7.3, 1.1, 1 H), 8.9 (dd, J = 8.6, 1.1, 1 H).

MS: m/z (%) = 320 (M$^+$, 100), 290 (M$^+$ –NO, 38), 244 (55), 200 (60).

Anal. Calc. for C$_{17}$H$_8$N$_2$O$_5$: C 63.75; H 2.50; N 8.75. Found: C 63.50; H 2.34; N 8.67.

3,9,11-Trinitro-7H-benz[d,e]anthracen-7-one (**5i**): yellow powder; mp > 300 °C.

IR (KBr): ν = 1660, 1541, 1522, 1508, 1346 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 8.1–8.2 (m, 2 H), 8.3 (d, J = 8.3, 1 H), 8.8 (d, J = 2.3, 1 H), 8.9–9.0 (m, 2 H), 9.5 (d, J = 2.3, 1 H).

MS: m/z (%) = 365 (M$^+$, 100), 319 (M$^+$ –NO, 43), 289 (40), 215 (67).

Anal. Calc. for C$_{17}$H$_7$N$_3$O$_7$; C 55.89; H 1.92; N 11.50. Found: C 55.86; H 1.90; N 11.36.

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(1) Paputa-Peck, M. C.; Marano, R. S.; Schuetzle, D.; Riley, T. L.; Hampton, C. V.; Prater, T. J.; Skewes, L. M.; Jensen, T. E.; Ruehle, P. H.; Bosch, L. C.; Duncan, W. P. *Anal. Chem.* **1983**, *55*, 1946.
(2) Handa, T.; Yamauchi, T.; Sawai, K.; Yamaura, T.; Koseki, Y.; Ishii, T. *Environ. Sci. Technol.* **1984**, *18*, 895.
(3) Nisioka, M. G.; Howard, C. C.; Contos, D. A.; Ball, L. M.; Lewtas, J. *Environ. Sci. Technol.* **1988**, *22*, 908.
(4) Kamens, R.; Bell, D.; Dietrich, A.; Perry, J.; Goodman, R.; Claxton, L.; Tejada, S. *Environ. Sci. Technol.* **1985**, *19*, 63.
(5) Tokiwa, H.; Ohnishi, Y. *CRC Crit. Rev. Toxicol.* **1986**, *17*, 23.
(6) Cho, B. P. *Org. Prep. Proc. Int.* **1995**, *27*, 243.
(7) Enya, T.; Suzuki, H.; Watanabe, T.; Hirayama, T.; Hisamatsu, Y. *Environ. Sci. Technol.*, in press.
(8) Pandit, P. N.; Tilak, B. D.; Venkataraman, K. *Proc. Ind. Acad. Sci.* **1952**, *35A*, 159; *Chem. Abstr.* **1953**, *47*, 8713.
(9) Shioda, H.; Kato, S. *Yuki Gosei Kagaku* **1957**, *15*, 361; *Chem. Abstr.* **1957**, *51*, 16393.
(10) Craig, J. T.; Woolhouse, A. D. *Aust. J. Chem.* **1971**, *24*, 835.
(11) Fanta, P. E. *Synthesis* **1974**, 9.
(12) Tucker, S. H.; Whalley, M. *J. Chem. Soc.* **1949**, 3213.
(13) Corey, E. J.; Székely, I.; Shiner, C. S. *Tetrahedron Lett.* **1977**, *40*, 3529.
(14) Hodgson, H. H.; Walker, W. *J. Chem. Soc.* **1933**, 1620.
(15) Price, C. C.; Voong, S. *Org. Synth. Coll. Vol. 3*, 664.
(16) Ward, E. R.; Pearson, B. D. *J. Chem. Soc.* **1959**, 3378.
(17) Hodgson, H. H.; Birtwell, S. *J. Chem. Soc.* **1944**, 75.
(18) James, C. W.; Kenner, J.; Stubbing, W. V. *J. Chem. Soc.* **1920**, *117*, 776.
(19) Goldstein, H.; Giddey, A. *Helv. Chim. Acta* **1954**, *37*, 1121.
(20) Summers, L. A.; Lehtonen, K. *Aust. J. Chem.* **1969**, *22*, 497.