2,4,5,7-Tetranitro-1,8-naphthalic Acid and Related Derivatives

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2,4,5,7-Tetranitro-1,8-naphthalic acid was prepared by oxidation of 3,5,6,8-tetranitroacenaphthene. Treatment of the acid with acetic anhydride produced 2,4,5,7-tetranitro-1,8-naphthalic anhydride. Reaction of the anhydride with methanol at room temperature, or with acid-catalyzed refluxing methanol gave rise to 2,4,5,7-tetranitro-1,8-monomethylnaphthalate. Treatment of 2,4,5,7-tetranitro-1,8-naphthalic anhydride with boiling methanol or ethanol resulted in decarboxylation and in the formation of the methyl and ethyl esters of 2,4,5,7-tetranitro-1-naphthoic acid, respectively. Reaction of 2,4,5,7-tetranitro-1,8-monomethylnaphthalate with diazomethane gave 2,4,5,7-tetranitro-1,8-dimethylnaphthalate. Displacement of one of the nitro groups by chlorine ensued when 2,4,5,7-tetranitro-1,8-naphthalic acid or the anhydride was treated with either acetyl chloride or thionyl chloride.

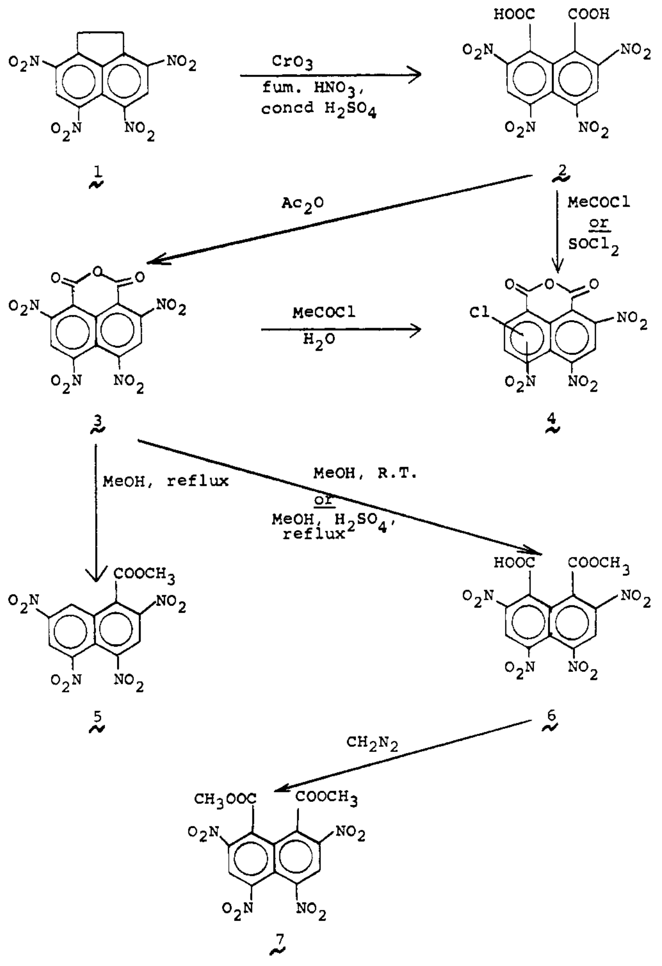
In connection with another study of aromatic polynitro compounds, it became necessary to prepare small amounts of the unknown 2,4,5,7-tetranitro-1,8-naphthalic acid (2). Attempts to obtain **2** by further nitrating 4,5-dinitro-1,8-naphthalic anhydride failed; only starting material was recovered. The desired tetranitronaphthalic acid has now been prepared via 3,5,6,8-tetranitroacenaphthene (**1**). The latter compound was obtained in 50–55% yields upon nitration of 5-nitroacenaphthene by a modification of the procedure of Vernon and Wilson (*4*) who reported the preparation of a tetranitro derivative of acenaphthene; however, neither yields nor chemical properties were given, and the 3,5,6,8-tetranitro isomer was assigned its structure on the basis of "electronic grounds" as described by Lumbroso (*2*). That the product of nitration of 5-nitroacenaphthene does indeed have the structure **1** has now been shown by elemental analysis and nmr spectroscopy. The nmr spectrum of a freshly prepared solution of **1** in CD_3CN exhibits two sharp singlets at τ 0.84 (aromatic protons) and τ 5.88 (aliphatic protons), in the ratio 1:2.

The synthesis and reactions of **2** are given in Scheme I.

Chromium trioxide oxidation of a solution of **1** in fuming nitric acid–concentrated sulfuric acid (1:1) gave **2** in 30–42% yields. Attempts to obtain **2** by bichromate oxidation in concentrated sulfuric acid alone failed, possibly because of the insolubility of **1** in the medium.

Treatment of **2** in acetic anhydride at reflux for 1.5 hr yielded the anhydride **3** in 75–90% yields. When this anhydride **3** is suspended in methanol at room temperature for 3–5 min, it affords the half ester **6** in 70% yield. The half ester **6** was also obtained when **3** was boiled for ca. 1 hr in methanol containing a few drops of concentrated sulfuric acid (50% yield). On the other hand, treatment of the anhydride **3** with methanol, in the absence of sulfuric acid, resulted in monodecarboxylation to give 2,4,5,7-tetranitro-1-methylnaphthoate (**5**) in 75% yield, and carbon dioxide was evolved. Under the same conditions, 4,5-dinitro-1,8-naphthalic anhydride failed to react and no CO_2 resulted. The propensity to CO_2 evolution in the reaction with anhydride **3** in ascribed to the presence of the 4 nitro groups whose activating effect on the rate of decarboxylation finds close parallel in the well-known easy loss of carbon dioxide from 2,4,6-trinitrobenzoic acid (*1*).

SCHEME I



Reaction of the half ester **6** with diazomethane gave the dimethyl ester **7** (60%); attempts to prepare **7** directly from the diacid **2** with diazomethane failed, possibly because of insolubility of the acid in diethyl ether used as solvent.

Treatment of acid **2** with refluxing $SOCl_2$ or acetyl chloride

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resulted in the formation of *x*-chloro-2,4-, *y*-trinitro-1,8-naphthalic anhydride (**4**). This replacement of one of the nitro groups by chlorine is ascribed to a nucleophilic displacement of an activated nitro function by hydrogen chloride generated during the reaction. The chloroanhydride **4** was obtained also when 2,4,5,7-tetranitro-1,8-naphthalic anhydride (**3**) was treated with acetyl chloride to which 3 mol-equiv of water (relative to **3**) had been added for the generation of HCl. In all cases, displacement of only one of the nitro functions took place, but no definite assignment was made concerning the position of attack. Analogous easy displacements of a nitro group by halogen have been observed recently by Shumov and co-workers (3) who studied the action of hydrohalic acids on tetranitrobenzene, tetranitrophenol, and tetranitroaniline.

EXPERIMENTAL

Melting points were taken on a "Melt-Pointer" Vanderkamp apparatus and are uncorrected. Infrared spectra were determined on a Perkin-Elmer Model 137 Infracord. Nmr spectra were obtained on a Varian A-60 instrument. Chemical shifts are reported in τ values relative to tetramethylsilane. All chemicals were reagent grade and were used as received, except acetyl chloride and thionyl chloride which were distilled before use.

3,5,6,8-Tetranitroacenaphthene (1). To a solution of 1 liter of fuming nitric acid (sp gr 1.50) and 1 liter of concentrated sulfuric acid cooled to about 5°C was added portionwise, so as to maintain the temperature below 20°C, 40.0 grams (0.201 mole) of 5-nitroacenaphthene. After complete addition, the solution was allowed to come to room temperature. The progress of the reaction was followed by melting point determinations and infrared analyses of aliquots, which indicated that the reaction was completed within 4 hr. The solution was poured into ice, the precipitate was collected, washed thoroughly with water, and dried. Recrystallization from glacial acetic acid gave 36.3 grams (54.1%) of pure **1**: mp 208–10°C dec; ir (Nujol), 3.1 μ (H aromatic), 6.1 μ (C aromatic), 6.4 and 7.4 μ (NO_2), and 11.5 μ (isolated H).

Anal. Calcd for $C_{12}H_6N_4O_8$: C, 43.12; H, 1.81; N, 16.77. Found: C, 43.20; H, 1.98; N, 16.68.

2,4,5,7-Tetranitro-1,8-naphthalic Acid (2). A solution of **1** (10.0 grams, 0.030 mole) in 50 ml of fuming nitric acid (sp gr 1.50) and 50 ml of concentrated sulfuric acid was treated over a 4-hr period with a solution of chromium trioxide (19.0 grams, 0.190 mole) in 40 ml of water, maintaining the temperature between 45–50°C. After complete addition, the reaction mixture was allowed to come to room temperature and was stirred for 18 hr. The suspension was poured onto ice. The solid was collected and washed with ice water to remove inorganic salts and dried. The crude material, 9.5 grams, was suspended in 50 ml of refluxing acetone and filtered while hot leaving 5.0 grams (42%) of 2,4,5,7-tetranitro-1,8-naphthalic acid (**2**). The acid has an ill-defined melting point, considerable darkening occurs at 250–5°C. A dta thermogram shows a sharp exotherm at 253°C; ir (Nujol), 3.1–3.2 μ (OH), 5.7 μ (C=O), 6.4 and 7.4 μ (NO_2), 8.2 μ (COC), and 10.9 μ (isolated aromatic CH).

Anal. Calcd for $C_{12}H_4N_4O_{12}$: C, 36.38; H, 1.02; N, 14.14. Found: C, 36.50; H, 1.28; N, 14.09.

Attempted oxidations in acetic acid at 80°C led to tarry products, while at room temperature no reaction occurred. Omitting sulfuric acid from the described procedure made the work-up of the product impracticable owing to the solubility of **2** in nitric acid.

2,4,5,7-Tetranitro-1,8-naphthalic Anhydride (3). A suspension of **2** (0.515 gram, 1.33 mmoles) in 5.0 ml of acetic anhydride was heated to reflux. The solution was refluxed for 1.5 hr, after which the solvent was distilled in vacuo. The last traces of acetic anhydride were removed by addition of 2 × 10 ml of cyclohexane and evaporation under vacuum. The crude solid was recrystallized from ethyl acetate–cyclohexane (3:1) to give 0.42 gram (85%) of **3**: mp 296°C dec; ir (Nujol), 5.55 and 5.70 μ (anhydride C=O) 6.45 and 7.45 μ (NO_2), and 9.3 μ (COC).

Anal. Calcd for $C_{12}H_2N_4O_{11}$: C, 38.11, H, 0.53; N, 14.82. Found: C, 38.30; H, 0.81; N, 14.68.

***x*-Chloro-2,4-, *y*-Trinitro-1,8-naphthalic Anhydride (4).** **(A) From 2,4,5,7-Tetranitro-1,8-naphthalic Acid (2).** A solution of **2** (0.300 gram, 0.76 mmole) in 5.0 ml of freshly distilled acetyl chloride was heated to reflux for 2 hr. The solvent was removed in vacuo leaving a solid residue (0.270 gram). Recrystallization from benzene–petroleum ether (3:1) afforded 0.245 gram (85.5%) of **4**: mp 282–4°C dec; ir (Nujol), 5.6 and 5.7 μ (anhydride C=O). The same product was also obtained when thionyl chloride was used instead of acetyl chloride.

Anal. Calcd for $C_{12}H_2N_3O_9Cl$: C, 39.20; H, 0.55; N, 11.43; Cl, 9.65. Found: C, 39.38; H, 0.82; N, 11.67; Cl, 9.89.

(B) From 2,4,5,7-Tetranitro-1,8-naphthalic Anhydride (3). A suspension of 0.500 gram (1.32 mmoles) of anhydride **3** in 3.0 ml of acetyl chloride to which had been added 0.0713 gram of water (3.96 mmoles) were stirred under reflux for 1 hr. The solvent was evaporated in vacuo, and the last traces of acetyl chloride were removed by vacuum codistillation with cyclohexane (2 × 10 ml). Purification as in A yielded the chlorotrinitroanhydride **4** (60%): mp 282–4°C dec.

Anal. Calcd for $C_{12}H_2N_3O_9Cl$: C, 39.20; N, 11.43; Cl, 9.65. Found: C, 39.43; N, 11.52; Cl, 9.36.

2,4,5,7-Tetranitro-1-methylnaphthoate (5). A mixture of anhydride **3** (0.378 gram, 1 mmole) and 10.0 ml of methanol was heated at reflux for 1 hr. The resulting carbon dioxide was collected in a saturated calcium hydroxide solution within minutes after heating. The solution was concentrated to ca. 5 ml, treated with decolorizing charcoal, and filtered. Removal of the solvent and recrystallization from methanol–water (1:1) gave 0.275 gram (75%) of the methyl ester **5**: mp 191°C; ir (Nujol), 5.78 μ (ester C=O), 6.5 and 7.4 μ (NO_2); nmr (CD_3CN) τ 5.83 (s, 3, COOCH_3), 0.84 (s, 2, aromatic H_3 and H_6), 0.91 (s, 1, H_8).

Anal. Calcd for $C_{12}H_6N_4O_{10}$: C, 39.36; H, 1.65; N, 15.30; mol wt 366. Found: C, 39.39; H, 1.47; N, 15.28; mol wt 360.

The ethyl ester of 2,4,5,7-tetranitro-1-naphthoic acid was obtained in a similar manner (60%) and exhibited the following properties: mp 153°C; nmr (CD_3CN) τ 8.53 (t, 3, $COOCH_2CH_3$), 5.31 (quartet, 2, $COOCH_2CH_3$), 0.84 (s, 2, aromatic H_3, H_6), and 0.91 (s, 1, H_8).

Anal. Calcd for $C_{13}H_8N_4O_{10}$: C, 41.06; H, 2.12; N, 14.74; mol wt 380. Found: C, 41.02; H, 2.29; N, 14.83; mol wt 382.

2,4,5,7-Tetranitro-1,8-monomethylnaphthalate (6). A suspension of anhydride **3** (0.500 gram, 1.32 mmoles) in 5 ml of methanol was allowed to stir for 5 min at room temperature. The suspension was filtered and the solid was dried, yielding 0.380 gram (70%) of **6**: mp 203–5°C dec; ir (Nujol), 2.8 μ (OH), 5.7 μ (C=O), 6.4 and 7.4 μ (NO_2), and 7.9–8.0 μ (COC).

Anal. Calcd for $C_{13}H_6N_4O_{12}$: C, 38.06; H, 1.47; N, 13.66. Found: C, 38.12; H, 1.62; N, 13.45.

Compound **6** was also obtained on refluxing for ca. 1 hr the anhydride **3** in methanol containing a few drops of sulfuric acid (58%): mp 203–5°C dec.

2,4,5,7-Tetranitro-1,8-dimethylnaphthalate (7). A solution of 0.15 gram of **6** (0.366 mmole) in 50 ml of tetrahydrofuran was added to an etheral solution (100 ml) of diazomethane derived from 2.6 grams (0.0121 mole) of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide. The reaction was maintained at 5°C in the dark for 18 hr, after which it was allowed to come to room temperature. The solvents were removed at ambient temperature under a stream of nitrogen, leaving 0.16 gram of crude material. The solid was recrystallized from methanol to give 0.093 gram (60%) of **7**: mp 281°C dec; ir (Nujol), 5.70 μ (C=O), 7.82 and 8.00 μ (COC).

Anal. Calcd for $C_{14}H_8N_4O_{12}$: C, 39.63; H, 1.90; N, 13.21. Found: C, 39.46; H, 2.05, N, 13.09.

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3,5-Dinitrobenzanilides

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3,5-Dinitrobenzanilides were prepared from 52 primary aromatic amines as the derivative of choice for characterization; 43 of these derivatives are new compounds.

In organic qualitative analysis, amides are the derivatives of choice for amines. Primary and secondary amines can be converted to carboxamides and sulfonamides by standard procedures (*3*). Despite the variety of choice, however, only the 3,5-dinitrobenzamide derivative combines the desirable characteristics of high melting points and easy recrystallizations throughout the range of aromatic amines. Although this derivative has been reported on occasion in the literature (*1*, *2*, *4*), no systematic compilation has been available. We have, therefore, characterized an extensive series of liquid and solid primary

Table I. 3,5-Dinitrobenzanilides of Liquid Primary Amines

Amine	Amine, bp, °C	Deriv. mp, °C[a]
Aniline	183	238.0–8.5[b]
3-Aminobenzotrifluoride	187	169.5–70.5
o-Toluidine	199	247.5–8.0[c]
m-Toluidine	203	263.0–3.5
o-Chloroaniline	207	208.0–8.5
2,4-Dimethylaniline	212	240.5–1.3
o-Ethylaniline	216	187.5–8.0[d]
p-Ethylaniline	216	223.5–4.2
2-Isopropylaniline	223	174.0–5.0
o-Anisidine	225	191.8–2.0
o-Bromoaniline	229	223.0–3.5
o-Phenetidine	229	162.0–2.5
m-Chloroaniline	230	228.5–9.0
m-Phenetidine	248	150.2–0.5
m-Anisidine	251	191.2–1.6
m-Bromoaniline	251	219.5–20.0
p-Phenetidine	254	230.5–1.0
2,6-Diisopropylaniline	257	276.0–7.0
Methyl anthranilate	260	154.0–6.0
Ethyl *m*-aminobenzoate	294	164.0–4.8

[a] Elemental analyses (C, H, N) in agreement with theoretical values were obtained and submitted for review. [b] Lit. mp 239°C; ref. *4*. [c] Lit. mp 241°C; ref. *1*. [d] Lit. mp 186°C; ref. *2*.

Table II. 3,5-Dinitrobenzanilides of Solid Primary Amine

Amine	Amine, mp, °C	Deriv. mp, °C[a]
m-Iodoaniline	27	226.5–7.5
2-Chloro-5-methylaniline	29	207.0–7.5
p-Toluidine	45	284.5–5.0[b]
2-Aminobiphenyl	45	182.5–3.2
3,4-Dimethylaniline	47	261.3–1.5
2,5-Dichloroaniline	50	190.0–0.5
α-Naphthylamine	50	274.0–4.5[c]
2,5-Dibromoaniline	51	205.5–6.5
m-Aminobenzonitrile	53	234.0–4.4
4-Aminobiphenyl	53	264.0–4.3
N,*N*-Dimethyl-*p*-phenylenediamine	53	282.5–3.5
o-Iodoaniline	56	244.5–5.0
p-Anisidine	57	244.0–4.5
p-Iodoaniline	62	253.0–4.0
2,4-Dichloroaniline	63	170.0–0.3
p-Bromoaniline	66	250.0–1.0[d]
p-Chloroaniline	70	236.0–6.7[e]
o-Nitroaniline	71	196.3–7.2
2,4,6-Trichloroaniline	77	232.0–3.0
2,4-Dibromoaniline	79	197.0–8.0
2,6-Dibromoaniline	83	314.5–5.5
p-Aminobenzonitrile	86	275.0–6.0
m-Aminobenzophenone	87	191.0–3.0
Ethyl *p*-aminobenzoate	89	190.2–0.8
o-Aminobenzophenone	105	226.0–6.8
p-Aminoacetophenone	106	205.0–6.0
β-Naphthylamine	112	340.0–1.0
m-Nitroaniline	114	209.0–10.0
p-Aminobenzophenone	124	245.5–6.3
p-Aminoazobenzene	126	244.0–5.0
p-Nitroaniline	147	282.0–2.5[f]
2,4-Dinitroaniline	180	213.5–14.0[g]

[a] Elemental analyses (C, H, N) in agreement with theoretical values were obtained and submitted for review. [b] Lit. mp 284°C; ref. *4*. [c] Lit. mp 268°C; ref. *1*. [d] Lit. mp 251°C; ref. *4*. [e] Lit. mp 237°C; ref. *4*. [f] Lit. mp 280°C; ref. *4*. [g] Lit. mp 213°C; ref. *4*.

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