A Facile Conversion of Dinitrotetramethylbenzenes into Dinitrotrimethylbenzaldehydes

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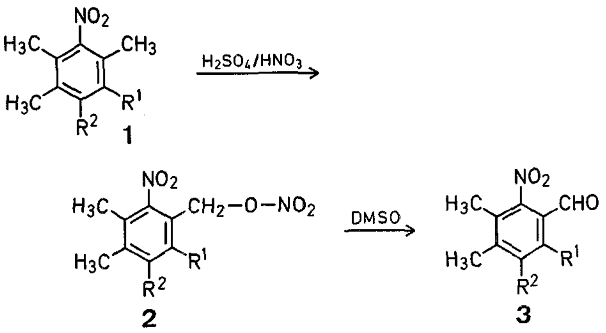
Dinitration of trimethylbenzaldehydes usually leads to either displacement of the formyl group by a nitro group, or extensive substitution on the alkyl side chain. However, some dinitrotrimethylbenzaldehydes were found to be conveniently prepared from dinitrotetramethylbenzenes.

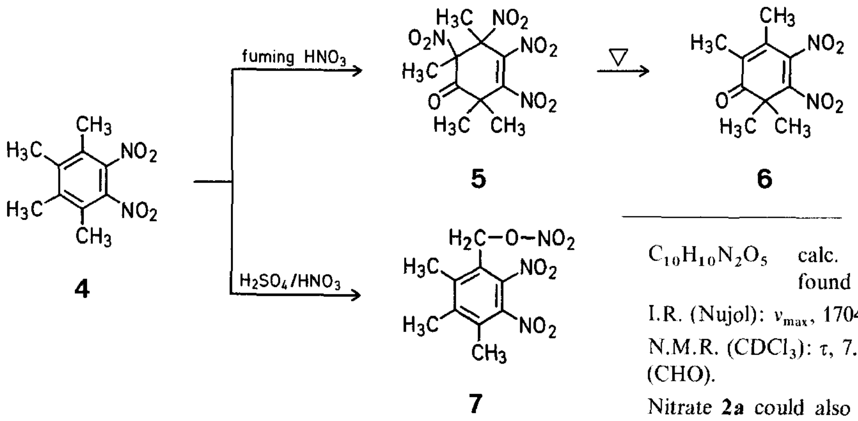
When 3,6-dinitro-1,2,4,5-tetramethylbenzene (dinitrodurene, **1a**) was dissolved in an excess of warm mixed acid [H_2SO_4:HNO_3 (d=1.5)=1:1], side-chain nitrooxylation soon took place to give 3,6-dinitro-2,4,5-trimethylbenzyl nitrate (**2a**) in 63–73% yield. Heating of **2a** in dimethyl sulfoxide containing a small amount of water and recrystallization of the resultant product from methanol yielded 3,6-dinitro-2,4,5-trimethylbenzaldehyde (**3a**; 74–80 %). The reaction was clean and the product was quite easy to purify. Similarly, a solution of 4,6-dinitro-1,2,3,5-tetramethylbenzene (dinitroisodurene, **1b**) in mixed acid, upon standing at room temperature, soon precipitated 2,6-dinitro-3,4,5-trimethylbenzyl nitrate (**2b**; 83%), which was treated with dimethyl sulfoxide to give 2,6-dinitro-3,4,5-trimethylbenzaldehyde (**3b**) in 78% yield. These aldehydes were stable in air but became colored on storage under diffused light.

Compound **1b** could be directly converted into **3b** (77–84%) by dissolving it in cold fuming nitric acid and allowing the solution to stand at room temperature for several days. In this case, the product was accompanied by small amounts of 2,6-dinitro-3,4,5-trimethylbenzoic acid and 2,6-dinitro-3,4,5-trimethylphenylnitromethane. Preferential oxidation occurred at the methyl group flanked both sides by nitro groups[1].



a $R^1 = CH_3$; $R^2 = NO_2$
b $R^1 = NO_2$; $R^2 = CH_3$

The side-chain nitrooxylation seems to be rather sensitive to the type of substitution on the aromatic ring as well as the nitrating agent used. Thus, the action of mixed acid upon 5,6-dinitro-1,2,3,4-tetramethylbenzene (dinitroprehnitene **4**) at low temperature gave 5,6-dinitro-2,3,4-trimethylbenzyl nitrate (**7**), while treatment of **4** with excess fuming nitric acid at room temperature yielded 2,3,4,5-tetranitro-2,3,6,6-tetramethylcyclohex-4-enone (**5**; 79–85%). Heating **5** in carbon tetrachloride at 50–60° readily eliminated two molecules of nitrogen dioxide, giving 4,5-dinitro-2,3,6,6-tetramethylcyclohexa-2,4-dienone (**6**)[2]. The structures of these carbonyl compounds were determined by elemental analyses, I.R., U.V., mass, and ^{1}H-N.M.R. spectra. Since the reaction seems to possess some synthetic utility, its scope is being investigated.



Melting points are uncorrected. ^{1}H-N.M.R. spectra were obtained in deuteriochloroform using a JEOL PS-100 spectrometer with TMS as internal standard. I.R. spectra were recorded in Nujol using a Jasco DS-402G spectrophotometer. U.V. spectra were measured in methanol with a Shimadzu QV-50 spectrophotometer.

3,6-Dinitro-2,4,5-trimethylbenzyl Nitrate (2a):

Finely powdered dinitrodurene (**1a**; 4.0 g) was added all at once to mixed acid [H_2SO_4:HNO_3 (d=1.5)=1:1; 30 ml] at 40° and the mixture was rapidly stirred. The solution soon became dark red and the temperature rose to 70–80° with gentle liberation of nitrogen dioxide. On cooling, the mixture was poured onto crushed ice and the white precipitate was collected by filtration, washed thoroughly with water, sucked as dry as possible, and crystallized from methanol/carbon tetrachloride (1:2; 60 ml); yield: 3.7 g (73%); m.p. 139–140°.

$C_{10}H_{11}N_3O_7$	calc.	C 42.11	H 3.89	N 14.73
	found	41.93	3.60	14.57

I.R. (Nujol): ν_{max}, 1645, 1273, 853 (ONO_2); 1535, 1365 (NO_2).

N.M.R. ($CDCl_3$): τ, 7.73 ($2CH_3$), 7.65 (CH_3), 4.59 (CH_2).

2,6-Dinitro-3,4,5-trimethylbenzyl Nitrate (2b):

A solution of dinitroisodurene (**1b**; 3.0 g) in mixed acid (see above; 30 ml) was allowed to stand at room temperature. A light yellow crystalline solid soon began to separate; this was collected and crystallized from dichloromethane/light petroleum; yield: 3.2 g (83%); m.p. 112–113°.

$C_{10}H_{11}N_3O_7$	calc.	C 42.11	H 3.89
	found	42.25	3.68

I.R. (Nujol): ν_{max}, 1660, 1275, 854 (ONO_2); 1537, 1362 (NO_2).

N.M.R. ($CDCl_3$): τ, 7.76 ($2CH_3$), 7.65 (CH_3), 4.70 (CH_2).

5,6-Dinitro-2,3,4-trimethylbenzyl Nitrate (7):

This compound was prepared from dinitroprehnitene (**4**) in a similar manner; yield 62%; m.p. 130–131° (from benzene).

$C_{10}H_{11}N_3O_7$	calc.	C 42.11	H 3.89
	found	42.26	4.05

I.R. (Nujol): ν_{max}, 1632, 1277, 858 (ONO_2); 1536, 1363 (NO_2).

N.M.R. ($CDCl_3$): τ, 7.72 (CH_3), 7.61 (CH_3), 7.57 (CH_3), 4.39 (CH_2).

3,6-Dinitro-2,4,5-trimethylbenzaldehyde (3a):

Several drops of water were added to a solution of nitrate **2a** (3.0 g) in dimethyl sulfoxide (10 ml) and the mixture was heated under gentle reflux for ~1 hr. The light yellow solution was then diluted with water and the white precipitate was collected by filtration, washed with water, and crystallized from methanol to give aldehyde **3a** as pale yellow needles; yield: 1.6–2.0 g (64–80%); m.p. 187–188°.

$C_{10}H_{10}N_2O_5$	calc.	C 50.42	H 4.23
	found	50.50	4.09

I.R. (Nujol): ν_{max}, 1704 (CO); 1531, 1369, 854 (NO_2).

N.M.R. ($CDCl_3$): τ, 7.75 (CH_3), 7.70 (CH_3), 7.49 (CH_3), −0.13 (CHO).

Nitrate **2a** could also be converted into **3a** by heating it with excess sulfuric acid at 50–60° but the product usually contained a substantial amount of 3,5,6-trinitro-1,2,4-trimethylbenzene.

2,6-Dinitro-3,4,5-trimethylbenzaldehyde (3b):

From **2b**: Nitrate **2b** (1.48 g) was treated with hot dimethyl sulfoxide as described above to give **3b** as nearly colorless prisms; yield: 0.96 g (78%); m.p. 162–164°.

$C_{10}H_{10}N_2O_5$	calc.	C 50.42	H 4.23
	found	50.12	4.29

I.R. (Nujol): ν_{max}, 1712 (CO); 1532, 1359, 861 (NO_2).

N.M.R. ($CDCl_3$): τ, 7.66 ($2CH_3$), 7.52 (CH_3), 0.16 (CHO).

From **1b**: A solution of **1b** (7.2 g) in fuming nitric acid (d=1.5; 60 ml), was allowed to stand at room temperature, and soon began to liberate red fumes. After the reaction had ceased, the solution was diluted with water and the white precipitate was filtered off, washed with dilute aqueous sodium hydrogen carbonate, and recrystallized from a mixture of dichloromethane and light petroleum; yield: 5.9–6.4 g (77–84%); m.p. 162–164°.

A small amount of *2,6-dinitro-3,4,5-trimethylphenylnitromethane*, m.p. 158–159°, and *2,6-dinitro-3,4,5-trimethylbenzoic acid*, m.p. 233–236° (dec.), were obtained as by-products.

2,3,4,5-Tetranitro-2,3,6,6-tetramethylcyclohex-4-enone (5):

Dinitroprehnitene (**4**; 7.5 g) was dissolved in cold fuming nitric acid (d=1.5; 60 ml) to give a yellow solution the color of which gradually turned dark red, and nitrogen dioxide began to evolve slowly. The mixture was allowed to stand at room temperature for several days, during the course of which the initial dark color faded to light yellow. On diluting with water, a pasty precipitate was obtained, which was thoroughly washed with water and dissolved in a minimum amount of dichloromethane. The solution was warmed at 35–40°, light petroleum (b.p. 40–50°) was added until the solution became slightly cloudy, and the solution was left to stand under cover. Ketone **5** soon began to crystallize as faintly yellow prisms; yield: 8.8–9.4 g (79–85%). It was thermally unstable and melted at 111–114° with complete decomposition.

$C_{10}H_{12}N_4O_9$	calc.	C 36.16	H 3.64	N 16.87	O 43.34
	found	36.23	3.58	16.76	43.37

I.R. (Nujol): ν_{max}, 1742 (CO); 1674 (C=C); 1540–1580, 1328–1337, 846 (NO_2).

N.M.R. ($CDCl_3$): τ, 8.71 (CH_3), 8.51 (CH_3), 8.11 (CH_3), 7.67 (CH_3).

U.V. (methanol): No maximum above 220 nm.

M.S.: *m/e*, 286 (M^+ —NO_2), 256 (M^+ —NO_2, —NO).

4,5-Dinitro-2,3,6,6-tetramethylcyclohexa-2,4-dienone (6):

This compound was formed with evolution of nitrogen dioxide by dissolving **5** in hot carbon tetrachloride; bright yellow prisms, m.p. 94–96°.

$C_{10}H_{12}N_2O_5$	calc.	C 50.00	H 5.04
	found	49.92	5.02

I.R. (Nujol): ν_{max}, 1684, 1644 (CO); 1617 (C=C); 1533–1543, 1365, 849 (NO_2).

N.M.R. ($CDCl_3$): τ, 8.56 ($2CH_3$), 7.94 (CH_3), 7.81 (CH_3).

U.V. (methanol): 296–298 nm (log = 3.66).

M.S.: *m/e*, 240 (M^+).

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[1] High regiospecificity for side-chain attack has been observed in the nitration of polyalkylbenzenes and their derivatives.
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[2] Details of structural proofs of these unsaturated cyclic ketones will be published in Bull. Chem. Soc. Japan.