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Pentanitro- and pentanitronitroso-2,4,6,8,10,12-hexaazaisowurtzitanes

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Reduction of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane with a sub-stoichiometric amount of SnCl$_2$ afforded a mixture of isomeric 2,4,6,8,10- and 2,4,6,8,12-pentanitro-2,4,6,8,10,12-hexaazaisowurtzitanes, their ratio depending on the solvent used. Treatment of these compounds with NOBF$_4$ gave rise to isomeric pentanitronitroso-2,4,6,8,10,12-hexaazaisowurtzitanes, which can be transformed into the starting NH products by treating with HCl.

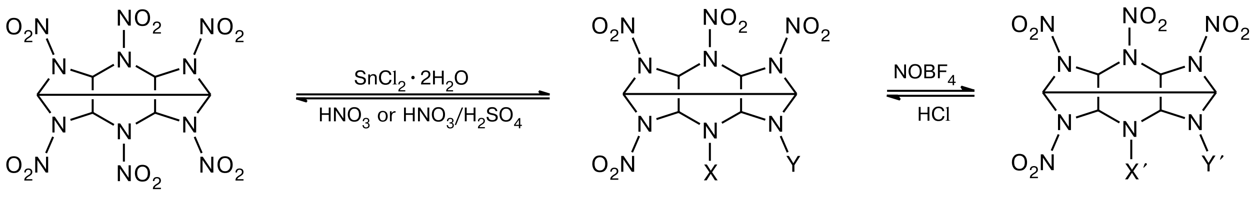
Key words: 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane, 2,4,6,8,10-pentanitro-2,4,6,8,10,12-hexaazaisowurtzitane, 2,4,6,8,12-pentanitro-2,4,6,8,10,12-hexaazaisowurtzitane, 2,4,6,8,10-pentanitro-12-nitroso-2,4,6,8,10,12-hexaazaisowurtzitane, 2,4,6,8,12-pentanitro-10-nitroso-2,4,6,8,10,12-hexaazaisowurtzitane, *N*-nitro compounds, *N*-nitroso compounds, tin chloride, reduction, *N*-nitrosation, *N*-NO-denitrosation, *N*-nitration.

The synthesis of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane[1] (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]dodecane or 1,3,4,7,8,10-hexanitrooctahydro-5,2,6-(iminomethenimino)-1*H*-imidazo[4,5-*b*]pyrazine, compound CL-20) (**1**) has been the greatest achievement in the chemistry of energetic compounds over the last two decades.

Compound CL-20 considerably surpasses the most powerful conventional explosive, *viz.*, octogene, in the energetic potential. In addition, it possesses an acceptable complex of operating characteristics. The synthesis of CL-20 has attracted considerable interest of experts and has given an impetus to extensive studies aimed at developing rational procedures for its preparation and investigating the properties of both the individual compound and composites on its basis. More than 350 publications on this problem can be found in the literature. Some other polynitro derivatives of hexaazaisowurtzitane, primarily, pentanitrohexaazaisowurtzitanes, are also of obvious interest. In particular, the latter can behave as powerful energetic materials and serve as the starting compounds for the synthesis of other polynitro derivatives containing the hexaazaisowurtzitane cage. Unlike CL-20, brief data on pentanitrohexaazaisowurtzitanes were reported only in two publications.[2,3] Reduction of CL-20 was reported[2] to give 2,4,6,8,10-pentanitro-2,4,6,8,10,12-hexaazaisowurtzitane (**2a**) in a maximum yield of 37% along with products of more profound transformations. In another study,[3] the second isomer, *viz.*, 2,4,6,8,12-pentanitro-2,4,6,8,10,12-hexaazaisowurtzitane (**2b**), was prepared by ethanolysis of 2,4,6,8,12-pentanitro-10-trifluoroacetyl-2,4,6,8,10,12-hexaazaisowurtzitane and characterized.

We investigated reduction of CL-20 and some transformations of reduction products in more detail. As in the earlier study,[2] we examined primarily tin(II) chloride as a reducing agent. However, we found that reduction with this reagent afforded a mixture of both possible isomeric products **2a** and **2b** (Scheme 1).

Scheme 1



1 (CL-20)

2a,b

2a: X = NO$_2$, Y = H
2b: X = H, Y = NO$_2$

3a,b

3a: X′ = NO$_2$, Y′ = NO
3b: X′ = NO, Y′ = NO$_2$

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Table 1. Conditions of reduction of CL-20 and the yields of pentanitrohexaazaisowurtzitanes **2a** + **2b**

CL-20/g	$SnCl_2 \cdot 2H_2O$/g	Solvent/mL	τ/h	Yield of **2a** + **2b**/g	Recovery of CL-20/g	Yield of **2a** + **2b** (%)[a]
0.5	0.5	MeOH, 25	0.5	0.15	0.18	52
0.5	0.5	MeOH, 25	1.25	0.07	0.01	15.9
0.5	1	MeOH, 25[b]	1	0.24	0.07	63
0.5	0.75	AcOH, 16.5	18	0.1	0.1	28
0.5	0.5	AcOH, 25	1	0.14	0.27	70
0.5	0.75	AcOH, 30[c]	1.5	0.22	0.11	62.8
0.5	0.5	AcOH, 15[d]	1	0.07	0.26	33
0.5	0.5	AcOH, 33—CF_3COOH, 6	1	0.1	0.27	50
0.5	0.5	AcOEt, 10	1	0.18	0.21	69
0.5	0.5	THF, 10	1	0.25	0.17	84.5
1	1	THF, 10	1	0.54	0.24	79.5
0.5	0.5	Dioxane, 30	1	0.12	0.25	54.5

[a] With respect to the consumed CL-20.
[b] In the presence of NaOH (0.03 g).
[c] AcOH was saturated with HCl for 30 min.
[d] In the presence of concentrated HCl (1 mL).

The total yield of isomers **2a** and **2b** depends substantially on the reaction conditions, primarily, on the ratio between the starting reagents, the reaction time, and the solvent used. In some cases, the yield achieved was higher than 80% (with respect to the consumed CL-20) (Table 1).

The formation of **2a** and **2b** was concluded from the ^{1}H and IR spectra and elemental analysis (for an isomeric mixture and individual compound **2b**) and based on certain transformations.

The isomer ratio was judged from the ^{1}H NMR spectra. It was found that this ratio depends substantially on the solvent used in the reduction. The isomer ratio can be changed severalfold by varying the solvent to prepare any isomer as the major product (Table 2).

Isomeric pentanitrohexaazaisowurtzitanes are white powders, which do not melt. At temperatures above 150 °C, these compounds decompose. The isomeric mixture gives one spot in TLC on silica gel, which precludes the use of chromatography for the separation of the isomers.

Table 2. Influence of solvents on the **2a** : **2b** ratio prepared by reduction of CL-20

Solvent	Ratio **2a** : **2b**
MeOH	1 : 0.6
MeOH[a]	1 : 1
AcOEt	1 : 1
Dioxane	1 : 1.16
THF	1 : 1.2
AcOH	1 : 2.2
AcOH[b]	1 : 2.25

[a] In the presence of NaOH.
[b] In the presence of concentrated HCl.

Nitration of an isomeric mixture with a sulfuric acid—nitric acid mixture or concentrated nitric acid afforded CL-20 as virtually the only reaction product (~80% yield) (see Scheme 1).

Isomers of pentanitrohexaazaisowurtzitane are readily nitrosated with nitrosonium tetrafluoroborate to form the corresponding, hitherto unknown pentanitronitroso derivatives of hexaazaisowurtzitane, *viz.*, **3a** and **3b**, in a total yield of up to 90% (see Scheme 1).

The nitroso derivatives thus formed are slightly yellowish powders, which decompose at temperatures below their melting points. Like the NH derivatives, these compounds give one spot in TLC on silica gel. It should be noted that the ^{1}H NMR spectrum of a mixture of isomers **3a** and **3b** overlaps with that of individual compound **3b**, which makes it impossible to judge their ratio in the mixture by NMR spectroscopy. This problem can be solved by transforming the nitroso derivatives into pentanitrohexaazaisowurtzitanes, which are easily distinguishable in their ^{1}H NMR spectra. This transformation proceeds readily to give the products in high yields (1 h, 20 °C, the yield is higher than 90%) by saturating a solution of the nitroso derivatives in inert solvents with hydrogen chloride. It was found that isomer **2b** is nitrosated several times more rapidly than **2a**. This fact along with the difference in the denitrosation rates of the isomers allows one to enrich and separate **2a** and **2b**. For example, the nitrosation—denitrosation cycle repeated twice enabled us to prepare **2b** in satisfactory yield (the percentage of the major component in the resulting mixture was no lower than 95%) from a ≈1 : 1 mixture of isomers **2a** and **2b**.

In addition to $SnCl_2 \cdot 2H_2O$, we used a zinc dust and an iron powder for the reduction of CL-20. However, these attempts did not give satisfactory results.

To summarize, reduction of CL-20 with a sub-stoichiometric amount of $SnCl_2$ was found to afford isomeric pentanitrohexaazaisowurtzitanes **2a** and **2b** as the major products. The isomer ratio depends substantially on the solvent used in the reduction and can be changed severalfold to give any of the above isomers as the major product. Isomeric pentanitronitrosohexaazaisowurtzitanes **3a** and **3b** were prepared for the first time by nitrosation of **2a** and **2b**. The nitrosation rate of compound **2b** is several times higher than that of its isomer **2a**. Treatment of nitroso derivatives **3a** and **3b** with HCl led to recovery of the starting compounds **2a** and **2b** in high yields. It was demonstrated that mixtures of isomeric pentanitrohexaazaisowurtzitanes can be enriched and separated owing to the differences in the nitrosation and denitrosation rates.

Experimental

The IR spectra were recorded on a Specord IR-75 instrument in KBr pellets. The ^1H NMR spectra were measured on Bruker WM-250 and Bruker AM-300 instruments. The course of the reactions and purities of the products were monitored by TLC on Silufol UV-254 plates. Compounds were isolated by preparative TLC using Silpearl silica gel with a luminophore in a 10 : 1 benzene—acetone system. Compound CL-20 was prepared by nitration of 2,6,8,12-tetraacetyl-2,4,6,8,10,12-hexaazaisowurtzitane.[4]

Reduction of 1,3,4,7,8,10-hexanitrooctahydro-5,2,6-(iminomethenimino)-1*H*-imidazo[4,5-b]pyrazine (1, CL-20). Tin(II) chloride dihydrate (0.5 g, 2.22 mmol) was added portionwise to a solution of nitro compound **1** (0.5 g, 1.14 mmol) in THF (10 mL) at 20 °C. The reaction mixture was stirred for 1 h and THF was distilled off. The residue was dissolved in AcOEt (35 mL), washed with 3*M* HCl (2×5 mL), water (3×5 mL), and brine (2×5 mL), and dried with Na_2SO_4. Then AcOEt was distilled off. Preparative TLC of the residue afforded the starting compound **1** (0.17 g) and a mixture of compounds **2a** and **2b** in a yield of 0.25 g (84% with respect to consumed nitro compound **1**). IR, ν/cm^{-1}: 1588, 1328 (NNO_2), 3390 (NH). ^1H NMR consists of a set of signals of **2a** (δ 5.35, br.t; 6.8, t; 7.2, t; 7.55, d; 7.7—8.4, m) and **2b** (δ 6.7, m; 7.85, s; 7.96, d) in a ratio of 1 : 1.2. Found (%): C, 18.88; H, 2.0; N, 39.46. $C_6H_7N_{11}O_{10}$. Calculated (%): C, 18.32; H, 1.78; N, 39.18.

Nitration of a mixture of 2,4,6,8,10-pentanitro-2,4,6,8,10,12-hexaazaisowurtzitane (2a) and 2,4,6,8,12-pentanitro-2,4,6,8,10,12-hexaazaisowurtzitane (2b). ***A.*** A mixture of compounds **2a** and **2b** (0.05 g) and 94% H_2SO_4 (0.25 mL) were added to 90% HNO_3 (0.75 mL) at 20 °C. The reaction mixture was stirred at 80—81 °C for 3 h, cooled, and poured onto ice. The precipitate that formed was filtered off, washed with water, and dried in air to give nitro compound **1** in a yield of 0.04 g (77%). ^1H NMR, δ: 8.33 (s, 4 H, CH); 8.18 (s, 2 H, CH).

B. A solution of a mixture of **2a** and **2b** (0.16 g) in 90% HNO_3 (10 mL) was kept at 20 °C for 1.5 h and then poured onto ice. The precipitate that formed was filtered off, washed with water, and dried in air to give compound **1** in a yield of 0.14 g (78.6%).

Nitrosation of a mixture of 2a and 2b. Nitrosonium tetrafluoroborate (0.09 g, 0.77 mmol) was added to a solution of a mixture of **2a** and **2b** (0.1 g, 0.25 mmol) in anhydrous CH_3CN (2 mL) at 20 °C. The reaction mixture was stirred at 20 °C for 1.5 h. A mixture of 2,4,6,8,10-pentanitro-12-nitroso-2,4,6,8,10,12-hexaazaisowurtzitane (**3a**) and 2,4,6,8,12-pentanitro-10-nitroso-2,4,6,8,10,12-hexaazaisowurtzitane (**3b**) was isolated by preparative TLC in a yield of 0.09 g (84%). IR, ν/cm^{-1}: 1610, 1340 (NNO_2). ^1H NMR, δ: 8.17 (s), 8.30—8.50 (m). Found (%): C, 17.94; H, 1.40; N, 40.0. $C_6H_6N_{12}O_{11}$. Calculated (%): C, 17.06; H, 1.42; N, 39.81.

Denitrosation of a mixture of 3a and 3b. Hydrogen chloride was passed through a solution of a mixture of **3a** and **3b** (0.17 g) in AcOEt (10 mL) for 1 h and then AcOEt was distilled off. A mixture of **2a** and **2b** was obtained in a yield of 0.15 g (94.9%). ^1H NMR (δ) consists of a set of signals of **2a** (5.35, br.t; 6.80, t; 7.20, t; 7.55, d; 7.70—8.40, m) and **2b** (6.70, m; 7.85, s; 7.96, d).

Isolation of compound 2b. Nitrosonium tetrafluoroborate (0.28 g, 2.39 mmol) was added to a solution of a mixture of **2a** and **2b** (in a ratio of 1 : 1.2; 0.78 g, 1.98 mmol) in anhydrous CH_3CN (16 mL) at 20 °C. The reaction mixture was stirred at 20 °C for 1.5 h, CH_3CN was partially distilled off, and a mixture of **3a** and **3b** was isolated by preparative TLC in a yield of 0.52 g. This mixture was dissolved in AcOEt (18 mL), HCl was passed through the solution for 1 h, and AcOEt was distilled off to give a mixture of **2a** and **2b** (0.38 g, 0.96 mmol). Nitrosonium tetrafluoroborate (0.13 g, 1.11 mmol) was added to a solution of this mixture in anhydrous CH_3CN (8 mL). The reaction mixture was stirred at 20 °C for 1.5 h, CH_3CN was partially evaporated, and a mixture of **3a** and **3b** was isolated from the residue by preparative TLC in a yield of 0.36 g. This mixture was dissolved in AcOEt (10 mL) and a solution of HCl in AcOEt (2 mL) was added. The mixture was kept at 20 °C for 15 min and concentrated to dryness. Compound **3b** was isolated by preparative TLC in a yield of 0.22 g. This product was dissolved in AcOEt (10 mL) and then HCl was passed through the solution for 1 h. Compound **2b** was isolated by preparative TLC in a yield of 0.15 g (37.7%). ^1H NMR, δ: 6.00 (br.s, 1 H, NH); 6.70 (m, 2 H, CH); 7.85 (s, 2 H, CH); 7.96 (d, 2 H, CH, J = 8 Hz). Found (%): C, 18.73; H, 1.80; N, 39.68. $C_6H_7N_{11}O_{10}$. Calculated (%): C, 18.32; H, 1.78; N, 39.18.

Nitrosation of 2b. Nitrosonium tetrafluoroborate (0.05 g, 0.43 mmol) was added to a solution of **2b** (0.14 g, 0.35 mmol) in anhydrous CH_3CN (3 mL). The reaction mixture was stirred at 20 °C for 1 h. Then CH_3CN was partially distilled off and compound **3b** was isolated from the residue by preparative TLC in a yield of 0.14 g (93%). IR, ν/cm^{-1}: 1610, 1340 (NNO_2). ^1H NMR, δ: 8.17 (s); 8.40—8.50 (m). Found (%): C, 18.04; H, 1.68; N, 39.58. $C_6H_6N_{12}O_{11}$. Calculated (%): C, 17.06; H, 1.42; N, 39.81.

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