

# 새 전구체에 의한 고폭화약 Hexanitrohexa-azaisowurtzitane(HNIW) 합성 연구

## Synthesis New Precursors for Hexanitrohexa-azaisowurtzitane(HNIW)

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### ABSTRACT

The hexanitrohexaazaisowurtzitane(HNIW) is a polycyclic caged nitramine oxidizer. For most existing weapons systems, the most critical ingredient in explosive and propellant applications is the oxidizer. HNIW, with its increase in performance output and energy capabilities for future in explosive and propellant systems.

Two new polyacylhexaazaisowurtzitanes were synthesized. Pentaacetylhexaaza-isowurtzitane(PAIW) or pentaacetylformylhexaazaisowurtzitane(PAFIW) can be a precursor in the preparation of HNIW, recently developed highly energetic material.

Key word : Polycyclic nitramine oxidizer, Hexanitrohexaazaisowurtzitane(HNIW), Pentaacetylhexaaza-isowurtzitane(PAIW), Pentaacetylformylhexaazaisowurtzitane(PAFIW)

### 1. introduction

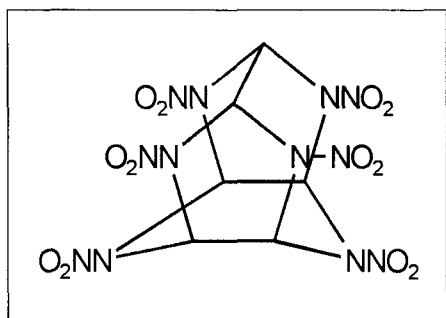
In a research effort, hexanitrohexaaza-isowurtzitane(HNIW, CL-20) (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo [5.5.0.0.5,9.0.3,11] dodecane, HNIW, CL-20, Fig. 1) has been developed as a new generation of explosives<sup>[1]</sup>.

A number of studies and calculation of HNIW

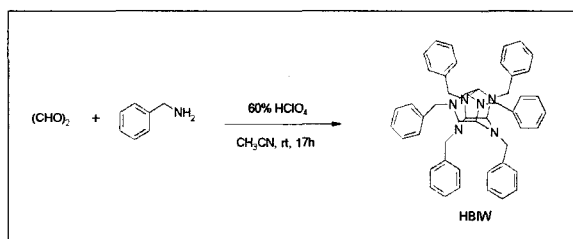
(Fig. 1) have been done for potential military applications<sup>[2,3]</sup>. The propellants or explosives composed of HNIW are expected to increase the performance in specific impulse, burn rate, ballistics and detonation velocity. From Kamlet formulas, using  $PM_3$  value heat of formation( $\Delta H$ ) of  $\beta$ -HNIW is 460.4KJ/mol, with the crystal density of 2.055g/cm<sup>3</sup>, with the detonation velocity of 9743m/s<sup>[2,3]</sup>.

HNIW was first known in 1986, but its synthesis was recently disclosed<sup>[1,4,5]</sup>. In its

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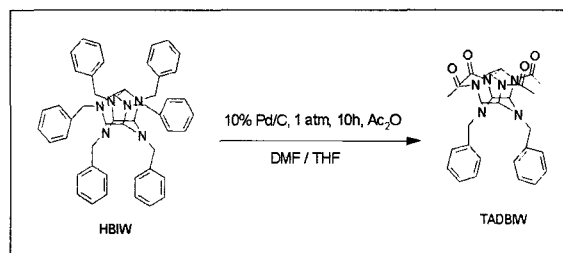
[Fig. 1] the structure of HNIW



[Fig. 2] HBIW is prepared from benzyl amine and glyoxal

multi-step synthesis, hexabenzylhexaazaisowurtzitane(HBIW, Fig. 2), prepared by the condensation of benzyl amine with glyoxal<sup>[6,7]</sup>, was the key intermediate.

Conversion of HBIW to HNIW has not been accomplished in one step. A nitro group at the nitrogen atom of an amine was generally introduced by the nitration of a secondary amine or by the nitrolysis of a N-acyl compound<sup>[8,9]</sup>. Hexaaza-isowurtzitane(IW, 3) has not been given by the hydrogenolysis of HBIW on 10% Pd/C<sup>[6,10]</sup>. HBIW was reacted with 2-trimethylsilylethyl chloroformate to give the corresponding hexaacylhexaaza iso-wurtzitane, but the yield was not known<sup>[4,11]</sup>.

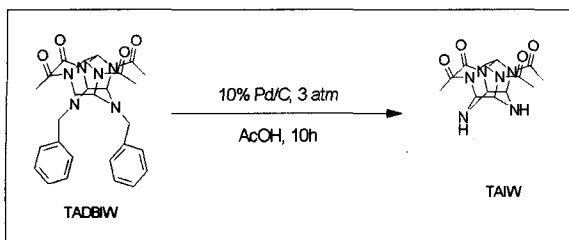


[Fig. 3] TADBIW is prepared from HBIW

In continuing efforts, researchers tried to replace benzyl group into acetyl one via debenzylacetylation. It was found that four out of six benzyl groups could be replaced by acetyl ones under the hydrogenolysis conditions, using acetic anhydride to give tetraacetyldibenzylhexaazaisowurtzitane(TADBIW, Fig. 3) in high yield<sup>[1,5,10,12]</sup>.

The remaining two benzyl groups are located at 4 and 10 positions. Direct conversion of TADBIW to HNIW could be done under a nitrolysis condition<sup>[10]</sup>, but the yield was too low.

In the previous syntheses of HNIW from TADBIW, the two benzyl groups were removed by hydrogenolysis or converted to other groups such as nitroso, formyl or acetyl<sup>[1,5,12]</sup>. Hydrogenolysis of TADBIW on 10% Pd/C gave tetraacetyl-hexaazaisowurtzitane(TAIW, Fig. 4) in acetic acid<sup>[5]</sup>, or tetraacetyldiformylhexaazaisowurtzitane(TADFIW, 6) in formic acid<sup>[12]</sup>. The treatment of TADBIW with NOBF<sub>4</sub> gave tetraacetyldinitrosohexaaza-isowurtzitane (TADNIW, 7), which was reported to be a precursor of HNIW<sup>[1]</sup>.



[Fig. 4] TAIW is prepared from TADBIW

Hexaacetylhexaazaisowurtzitane(HAIW, 8) was prepared by the reaction of TAIW with a mixture of acetic anhydride and acetyl chloride<sup>[5]</sup>. TAIW, TADFIW or HAIW may be converted to HNIW by the suitable reaction conditions.

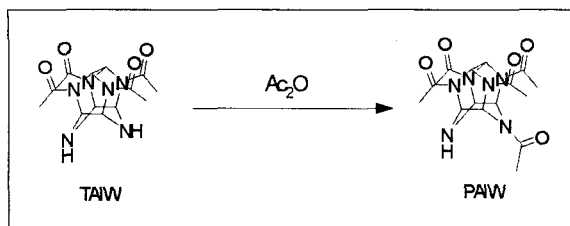
When TADBIW was hydrogenated on 10% Pd/C in the presence of a mixture of acetic acid and acetic anhydride, tetraacetyldiethylhexaazaisowurtzitane(TADEIW, 9) was obtained as a major compound. The benzyl groups in the six membered ring were converted to ethyl groups via debenzylacetylation followed by the reduction of the acetyl group, resulting in TADEIW which was failed to give HNIW<sup>[5,10]</sup>. There were some drawbacks in the preparation of HNIW from TAIW, TADFIW and HAIW. For examples, isolation of TAIW was not easy because of low solubility. A fire occurred in the preparation of TADFIW, when formic acid rapidly contacted with the Pd catalyst. HCl gas evolved in the preparation of HAIW.

In this paper, we describe the syntheses of other suitable precursors which are able to supplement the difficulties and the nitration conditions for HNIW.

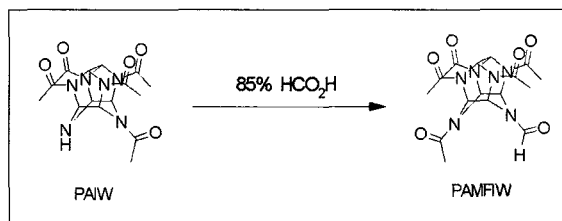
In the synthesis of HNIW from HBIW, direct conversion of the benzyl groups to nitro ones was in vain, since not only the cage structure was unstable under the nitrolysis conditions, but also some nitrations took place at the phenyl ring<sup>[13]</sup>. A compound having six acyl groups was thought to be a possible precursor for HNIW, like TADFIW and HAIW. In a course of debenzylacetylation, four benzyl groups may be replaced by acetyl groups, one by one<sup>[4]</sup>. If this actually happens, the mixture having Rf values between HBIW and TADBIW on TLC would be compounds with less than four acetyl groups. Trial of converting this mixture to compounds containing three or more formyl groups under the same reaction conditions for TADFIW has failed probably due to instability of the mixture under the acidic conditions.

## 2. Experimental

All chemicals were reagent grade(Aldrich Chemical Co.) and were used as purchased without further purification. TAIW was prepared by the literature procedure<sup>[5]</sup> and used in the further reaction without purification. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Gemini 2000(200MHz) spectrometer in CDCl<sub>3</sub> unless otherwise stated. Melting points were determined on a Yamato MP-21 and were uncorrected. Elemental analysis was performed by a Xytel



[Fig. 5] TAIW is prepared from PAIW

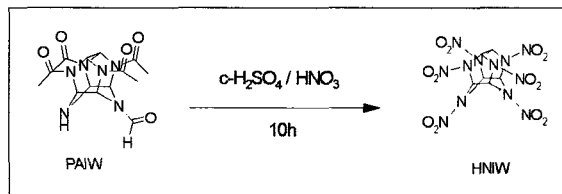


[Fig. 6] PAIW is prepared from PAFIW

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Pentaacetylhexaaza-isowurtzitane(PAIW, 9, Fig. 5). The mixture of TAIW(1.0 g, 2.95 mmol), acetic acid(15 mL) and acetic anhydride(10 mL) was heated for 12 h at 60°C. The resulting mixture was concentrated in vacuo and the residue was chromatographed on silica gel(10% MeOH/CH<sub>2</sub>Cl<sub>2</sub>) to give a white solid(1.06 g, 95%). m.p. 305~306°C(MeOH); <sup>1</sup>H-NMR δ1.95~2.16(m, 12H, CH<sub>3</sub>), 2.41(s, 3H, CH<sub>3</sub>), 3.40~ 3.57(m, 1H, NH), 5.36~5.70(m, 2H, CH<sub>2</sub>), 5.96~6.96(m, 4H, CH). <sup>13</sup>C-NMR δ18.8, 19.1, 19.2, 19.9, 20.5, 59.5, 62.9, 64.6, 65.4, 69.9, 70.1, 165.3, 166.0, 166.6, 170.0, 168.0. FT-IR(KBr) λ<sub>max</sub> 3477, 1659, 1408, 1311, 1163, 989 cm<sup>-1</sup>. EI-MS 378(M<sup>+</sup>, 20), 334(22), 293(52), 250(38), 208(100), 165(65), 123(60). Anal. Calcd for C<sub>16</sub>H<sub>22</sub>N<sub>6</sub>O<sub>5</sub> : C 50.79, H 5.86, N 22.21. Found: C 51.19, H 6.16, N 22.55.

Pentaacetylformylhexaaza-isowurtzitane(PAFIW, 11, Fig. 6). A solution of PAIW(1.0 g, 2.65 mmol) in 85% formic acid(10 mL) was heated for 4 h at 60°C. The resulting mixture was concentrated in vacuo and the residue was crystallized with



[Fig. 7] PAIW is prepared from HNIW

MeOH to give a white solid(1.02 g, 95%).

m.p. 201~202°C <sup>1</sup>H-NMR δ1.95~2.16(m, 12H, CH<sub>3</sub>), 2.41(s, 3H, CH<sub>3</sub>), 6.04~7.10(m, 6H, CH), 8.31(s, 1H, CHO). <sup>13</sup>C-NMR δ19.2, 20.0, 20.2, 58.7, 59.5, 64.7, 64.9, 70.5, 70.6, 159.8, 166.0, 166.2, 166.5, 166.8, 168.1. FT-IR(KBr) λ<sub>max</sub> 3038, 1668, 1405, 1303, 1163, 953 cm<sup>-1</sup>. EI-MS 406(M<sup>+</sup>, 17), 363(22), 335(13), 321(33), 293(25), 279(100), 237(19), 208(19), 195(11), 166(15), 123(24). Anal. Calcd for C<sub>17</sub>H<sub>22</sub>N<sub>6</sub>O<sub>6</sub> : C 50.24, H 5.46, N 20.68.

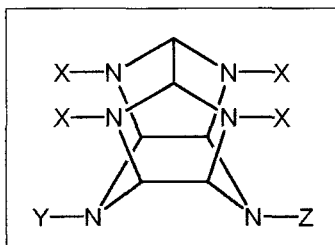
Found : C 50.25, H 5.42, N 20.71.

Nitrolysis of PAIW. After a mixture of PAIW (1.0 g, 2.65 mmol), c-HNO<sub>3</sub>(2 mL) and c-H<sub>2</sub>SO<sub>4</sub> (2 mL) was heated for 10 h at 60°C, the reaction mixture was poured into ice water and the precipitate was filtered to give HNIW(1.13 g, 97%). m.p.(230°C, decomposed) and spectral data were the same as those in the literature<sup>[1]</sup>.

Nitrolysis of PAFIW. According to the procedure described above, HNIW(96%) was obtained from PAFIW.

### 3. Results and Discussion

In the synthesis of HNIW from HBIW, direct conversion of the benzyl groups to nitro ones was in vain, since not only the cage structure was unstable under the nitrolysis conditions, but also some nitrations took place at the phenyl ring [13].



[Table 1] The summary of structure of hexaazaisowurtzitane

No.	X	Y	Z	Abbreviation
1	NO <sub>2</sub>	NO <sub>2</sub>	NO <sub>2</sub>	HNIW
2	CH <sub>2</sub> Ph	CH <sub>2</sub> Ph	CH <sub>2</sub> Ph	HBIW
3	H	H	H	IW
4	Ac	CH <sub>2</sub> Ph	CH <sub>2</sub> Ph	TADBIW
5	Ac	H	H	TAIW
6	Ac	CHO	CHO	TADFIW
7	Ac	NO	NO	TADNIW
8	Ac	Ac	Ac	HAIW
9	Ac	Et	Et	TADEIW
10	Ac	Ac	H	PAIW
11	Ac	Ac	CHO	PAFIW

A compound having six acyl groups as thought to be a possible precursor for HNIW, like TADFIW and HAIW. In a course of debenzylacetylation, four benzyl groups may be replaced by acetyl groups, one by one<sup>[4]</sup>. If this actually happens, the mixture having Rf values between HBIW and TADBIW on TLC would be compounds with less than four acetyl groups. Trial of converting this mixture to compounds containing three or more formyl groups under the same reaction conditions for TADFIW has failed probably due to instability of the mixture under the acidic conditions.

Due to the unsymmetrical structure, <sup>1</sup>H or <sup>13</sup>C NMR pattern of PAIW or PAFIW was much more complex than that of TAIW, HAIW or TADFIW. When TAIW was heated in the mixture of acetic acid, acetic anhydride and formic acid to prepare PAFIW in one step, TADFIW was exclusively prepared. TADFIW was also prepared rather than HAIW in the reaction of TAIW with the mixture of acetyl chloride and formic acid. The reaction of TAIW with ethyl chloroformate failed to give the corresponding hexaazaisowurtzitane. So the reactivity toward TAIW may be in order of formyl, acetyl and carbamate.

There have been many reagents for nitration or nitrolysis reactions<sup>[8,9,14]</sup>. Among those reagents, 100% HNO<sub>3</sub>, HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>-TFAA were attempted for HNIW. Only HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> was effective to give HNIW from PAIW or

PAFIW in high yield. We also studied the nitration step using NMR spectra. The proton peaks of the acetyl groups in PAIW or PAFIW appeared around 2.10 ppm representing the ones at the five membered rings as a multiplet and 2.41 ppm of the six membered ring as a singlet. During the nitration of PAIW, the peak intensity around 2.10 ppm was decreased faster than that of 2.41 ppm. In the nitration of PAFIW, formyl peak disappeared more slowly than the acetyl peak at 2.41 ppm. So the acetyl group at the five membered ring was reacted faster than that of the six membered ring, and the acetyl group was more reactive than the formyl one in the nitration.

In conclusion, PAIW and PAFIW could be employed in the preparation of HNIW as potential precursors in addition to TAIW, HAIW and TADFIW.

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