

Kyoo-Hyun Chung,* Hee-Sup Kil, In-young Choi, Chan-Kook Chu, and Ik-Mo Lee

Department of Chemistry, Inha University, Incheon 402-751, Korea
Received January 18, 2000

Two new polyacylhexaazaisowurtzitane were synthesized. Pentaacetyl- or pentaacetylformylhexaazaisowurtzitane can be a precursor in the preparation of HNIW, recently developed highly energetic material.

J. Heterocyclic Chem., **37**, 1647 (2000).

In a research effort, hexanitrohexaazaisowurtzitane (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, **1**) has been developed as a new generation of explosives [1]. A number of studies and calculations of HNIW have been done for potential military applications [2,3]. The propellants or explosives composed of HNIW are expected to increase the performance in specific impulse, burn rate, ballistics and detonation velocity.

HNIW was first known in 1986, but its synthesis was recently disclosed [1,4,5]. In its multi-step synthesis, hexabenzylhexaazaisowurtzitane (HBIW, **2**), prepared by the condensation of benzyl amine with glyoxal [6,7], 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 [8,9]. Hexaazaisowurtzitane (IW, **3**) has not been given by the hydrogenolysis of HBIW on 10% Pd/C [6,10]. HBIW was reacted with 2-trimethylsilylethyl chloroformate to give the corresponding hexaacylhexaazaisowurtzitane, but the yield was not known [4,11].

In continuing efforts, researchers tried to replace the benzyl group with an acetyl group *via* debenzylacetylation. It was found that four out of six benzyl groups could be replaced by acetyl groups under hydrogenolysis conditions, using acetic anhydride to give tetraacetyldibenzylhexaazaisowurtzitane (TADBIW, **4**) in high yield [1,5,10,12]. The remaining two benzyl groups are located at the 4 and 10 positions. Direct conversion of TADBIW to HNIW could be done under nitrolysis conditions [10], 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 [1,5,12]. Hydrogenolysis of TADBIW on 10% Pd/C gave tetraacetylhexaazaisowurtzitane (TAIW, **5**) in acetic acid [5], or tetraacetyldiformylhexaazaisowurtzitane (TADFIW, **6**) in formic acid [12]. The treatment of TADBIW with NOBF₄ gave tetraacetyldinitrosohexaazaisowurtzitane (TADNIW, **7**), which was reported to be a precursor of HNIW [1]. Hexaacylhexaazaisowurtzitane (HAIW, **8**) was prepared by the reaction of TAIW with a mixture of acetic anhydride and acetyl chloride [5]. TAIW, TADFIW or HAIW may be converted to HNIW by the suitable reaction conditions.

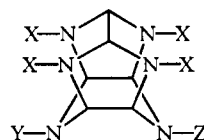
When TADBIW was hydrogenated on 10% Pd/C in the presence of a mixture of acetic acid and acetic anhydride, tetraacetyldiethylhexaazaisowurtzitane (TADEIW, **9**) was obtained as a major compound. The benzyl groups in the six membered ring were converted to ethyl groups *via* debenzylacetylation followed by the reduction of the acetyl group, resulting in TADEIW which failed to give HNIW [5,10]. There were some drawbacks in the preparation of HNIW from TAIW, TADFIW and HAIW. For example, 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 that are able to supplement the difficulties and the nitration conditions for HNIW.

Results and Discussion.

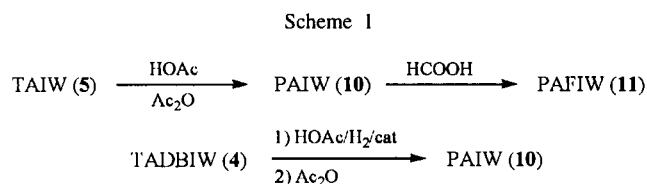
In the synthesis of HNIW from HBIW, direct conversion of the benzyl groups to nitro ones was in vain, since not only the cage structure was unstable under the nitrolysis conditions, but also some nitrations took place at the phenyl ring [13]. A compound having six acyl groups was thought to be a possible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

No.	X	Y	Z	Abbreviation
1	NO ₂	NO ₂	NO ₂	HNIW
2	CH ₂ Ph	CH ₂ Ph	CH ₂ Ph	HBIW
3	H	H	H	IW
4	Ac	CH ₂ Ph	CH ₂ 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



Next, we tried to synthesize pentaacetylhexaazaisowurtzitane (PAIW, **10**) and pentaacetylformylhexa-

azaisowurtzitane (PAFIW, **11**). PAIW might be obtained from TAIW under milder reaction conditions than HAIW. TAIW was reacted with a mixture of acetic acid and acetic anhydride to give PAIW. The reaction was rather slow and took about 12 hours at 60° for completion. The higher the reaction temperature, the more HAIW was formed, but obtained as a minor product. PAIW can also be obtained in one pot reaction by hydrogenolysis of TADBIW in acetic acid on 10% Pd/C followed by subsequent reaction with acetic anhydride. In this method, TADEIW was not given, but PAIW was easily separated from the solid catalyst, unlikely to TAIW. In the treatment of PAIW with formic acid, PAFIW was given within 4 hours at 60° (Scheme 1).



Due to the unsymmetrical structure, ^1H or ^{13}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 [8,9,14]. Among those reagents, 100% HNO_3 , $\text{HNO}_3\text{-H}_2\text{SO}_4$ and $\text{HNO}_3\text{-TFAA}$ were attempted for HNIW. Only $\text{HNO}_3\text{-H}_2\text{SO}_4$ 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, the formyl peak disappeared more slowly than the acetyl peak at 2.41 ppm. This shows that the acetyl group at the five membered ring reacts faster than that of the six membered ring, and the acetyl group is 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.

EXPERIMENTAL

All chemicals were reagent grade (Aldrich Chemical Co.) and were used as purchased without further purification. TAIW was prepared by the literature procedure [5] and used in further reactions without purification. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 2000 (200MHz) spectrometer in CDCl_3 unless otherwise stated. Melting points were determined on a Yamato MP-21 and were uncorrected. Elemental analysis was performed by a Xytel EA-1110 at Inha University.

2,4,6,8,12-Pentaacetyl-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]dodecane (PAIW, **9**).

The mixture of TAIW (1.0 g, 2.95 mmol), acetic acid (15 mL) and acetic anhydride (10 mL) was heated for 12 hours at 60°. The resulting mixture was concentrated *in vacuo* and the residue was chromatographed on silica gel (10% $\text{MeOH}/\text{CH}_2\text{Cl}_2$) to give a white solid (1.06 g, 95%); m.p. 305-306° (MeOH); ^1H NMR: δ 1.95-2.16 (m, 12H, CH_3), 2.41 (s, 3H, CH_3), 3.40-3.57 (m, 1H, NH), 5.36-5.70 (m, 2H, CH_2), 5.96-6.96 (m, 4H, CH); ^{13}C NMR: δ 18.8, 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_{max} 3477, 1659, 1408, 1311, 1163, 989 cm^{-1} . EI-MS 378 (M^+ , 20), 334 (22), 293 (52), 250 (38), 208 (100), 165 (65), 123 (60).

Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{N}_6\text{O}_5$: C 50.79, H 5.86, N 22.21. Found: C 51.19, H 6.16, N 22.55.

2,4,6,8,12-Pentaacetyl-10-formyl-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]dodecane (PAFIW, **10**).

A solution of PAIW (1.0 g, 2.65 mmol) in 85% formic acid (10 mL) was heated for 4 hours at 60°. The resulting mixture was concentrated *in vacuo* and the residue was crystallized with MeOH to give a white solid (1.02 g, 95%); m.p. 201-202°; ^1H NMR: δ 1.95-2.16 (m, 12H, CH_3), 2.41 (s, 3H, CH_3), 6.04-7.10 (m, 6H, CH), 8.31 (s, 1H, CHO). ^{13}C NMR: δ 19.2, 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_{max} 3038, 1668, 1405, 1303, 1163, 953 cm^{-1} . EI-MS 406 (M^+ , 17), 363 (22), 335 (13), 321 (33), 293 (25), 279 (100), 237 (19), 208 (19), 195 (11), 166 (15), 123 (24).

Anal. Calcd for $\text{C}_{17}\text{H}_{22}\text{N}_6\text{O}_6$: 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_3 (2 mL) and c- H_2SO_4 (2 mL) was heated for 10 hours at 60° then the reaction mixture was poured into ice water and the precipitate was filtered to give HNIW (1.13 g, 97%). m.p. (230°, decomposed) and spectral data were the same as those in the literature [1].

Nitrolysis of PAFIW.

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

Acknowledgment.

Financial supports from ADD, Inha University Fund (1998), and Brain Korea 21 are gratefully acknowledged.

REFERENCES AND NOTES

- [1] A. T. Nielsen, A. P. Chafin, S. L. Christian, D. W. Moore, M. P. Nadler, R. A. Nissan, and D. J. Vanderah, *Tetrahedron*, **54**, 11793 (1998).

- [2] D. Mueller, *Propellants, Explosives and pyrotechnics*, **24**, 176 (1999).
- [3] T. P. Russell, P. T. Miller, G. J. Piermarini and S. Block, *J. Phys. Chem.*, **97**, 1993 (1993).
- [4] T. Kodama, *Japan. Kokai Tokkyo JP*, 321962 (1994).
- [5] T. Kodama, M. Tojo and M. Ikeda, *PCT. Int. Appl. WO.*, 23792 (1996); *Chem. Abstr.*, **125**, 275920v (1996).
- [6] A. T. Nielsen, R. A. Nissan, D. J. Vanderah, C. L. Coon, R. D. Gilardi, C. F. George and J. Flippen-Anderson, *J. Org. Chem.*, **55**, 1459 (1990).
- [7] L. F. Cannizzo, W. W. Edwards, R. B. Wardle and T. K. Highsmith, *U.S.P.*, 5723604 (1998); *Chem. Abstr.*, **126**, 145956w (1997).
- [8] J. H. Robson, *J. Am. Chem. Soc.*, **77**, 107 (1955).
- [9] J. H. Robson and J. Reinhar, *J. Am. Chem. Soc.*, **77**, 2453 (1955).
- [10] A. J. Bellamy, *Tetrahedron*, **51**, 4711 (1995).
- [11] A. L. Cambell, D. R. Philipamskas, Z. K. Khana and R. A. Rhodeo, *Tetrahedron Lett.*, 2331 (1987).
- [12] R. B. Wardle and W. W. Edwards, *U.S.P.*, 5739325 (1998); *Chem. Abstr.*, **127**, 110983w (1997).
- [13] K.-H. Chung and S.-H. Chun, *Bull. Korean. Chem. Soc.*, **18**, 1317 (1997).
- [14] G. A. Olah, R. Malhotra and S. C. Narang, *Nitration Methods and Mechanisms*, VCH Publisher, New York, 1989, pp275-286.