NITRATION OF TAIW TO SYNTHESIZE CL-20 USING N_{2}O_{5}/HNO_{3} AS NITRATING AGENT

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ABSTRACT

CL-20 is usually prepared via nitration with the concentrated mineral acid as catalyst, but this technique is one of the most environmentally harmful processes. In this article, CL-20 was synthesized in a nitration of tetraacetylhexaazaisowurtzitane (TAIW) by using N_{2}O_{5}/HNO_{3} as the nitrating agent. The product yield can reach 86.1% and the purity is 99%. The structure of the compound was characterized by NMR, IR and MS. Meanwhile, the effects of reaction temperature, reaction time, and the molar ratio of reagents on the yield were also investigated. The experimental results showed the optimal reaction conditions are reaction temperature 40°C, reaction time 1h, and the molar ratio of TAIW: N_{2}O_{5}: HNO_{3} being 1:4:36. Meanwhile, the crystal formation and nitration mechanism were also discussed.

Keywords CL-20, dinitrogen pentoxide, nitration, nitration, explosive

INTRODUCTION

Hexanitrohexaazaisowurtzitane (CL-20), a high energy material with cage structure, is considered the most powerful explosive today. Its attributes of great interest are high density (> 2 g·cm⁻³), due to cage structure, and positive heat of formation of the order of 419 kJ·mol⁻¹ because of typical structure features including ring strain. CL-20 is envisaged to deliver 14%-20% higher performance than 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX). Its production technology is studied all over the world.

All known methods of producing CL-20 are based on the same starting material, hexabenzyllhexaazaisowurtzitane (HBIW), which can be reductively acylated to form tetraacetyldibenzyllhexaazaisowurtzitane (TADBIW). The benzyl groups can then be removed or changed by other groups, with the formation of tetraacetyldiformylhexaazaisowurtzitane(TADFIW), tetraacetyldiethylhexaazaisowurtzitane (TADEIW), tetraacetylhexaazaisowurtzitane (TAIW), or hexaacetylhexaazaisowurtzitane (HAIW). The conversion of HBIW directly to CL-20 is one of the major challenges faced by the HEMs community. Reaction of HBIW with N_{2}O_{5} enriched HNO_{3} led to the formation of low melting compound. The IR spectra of the product indicated the cleavage of the cage structure. Subsequently, well reported precursor TADBIW obtained by reductive debenzylation of HBIW was subjected to nitration by N_{2}O_{5}. Nitrination of TADBIW in N_{2}O_{5} enriched HNO_{3} yielded a product, which could be resolved into three components by thin layer chromatography (TLC). The components were separated on column. IR revealed the presence of both C-NO_{2} and N-NO_{2} suggesting that nitration of both isowurzitane nitrogen as well as phenyl ring. Consequently, completely debenzylated precursor TAIW was selected for N_{2}O_{5} nitration.

In this paper, one-step reaction from TAIW to CL-20 can be finished with higher yield and purity using N_{2}O_{5}-HNO_{3} as nitrating agent. This technics not only enhances the yield, but also avoids the use of mixture of concentrated nitric and sulfuric acid as nitrating agent, which accords with the demand of environmental protection.
EXPERIMENTAL

Chemicals and Equipments
Dinitrogen pentoxide was prepared by the reaction of N$_2$O$_4$ with ozone$^{11}$ and stored at -20°C before use. TAIW was prepared by reductive acetylation of TADBIW$^{12}$, and its purity was more than 98% (tested by $^1$HNMR), it was directly used without further purification. Other chemicals were of research grade and were used as obtained from J&K Co. Ltd.$^1$HNMR spectra was recorded on Bruker DRX 300MHz. IR spectra was recorded on MB154S FTIR using KBr pellets. Mass spectra was recorded on Finnigan TSQ Quantum ultra AM LC/MS spectrometer.

Typical Procedure for Nitration
TAIW (3 g) was added to dinitrogen pentoxide (4.3 g) dissolved in 98% nitric acid (15 ml) cooled down to 0°C in a round bottom flask fitted with a guard tube and nitrogen purging assembly. The mixture was stirred for 1 h at 40°C, and then heated to 90°C for 2 h. After reaction, the mixture was poured to 100 ml ice water, cooling and crystallizing. After filtrating and drying, CL-20 was obtained and analysed by LC/MS.

$^1$H-NMR (CD$_3$COCD$_3$) $\delta$/ppm: 8.37 (s, 4H, CH), 8.24 (s, 2H, CH); IR/cm$^{-1}$: 3028, 2882, 1592, 1510, 1282, 1044, 962, 872, 750, 714, 666, 568; MS/%: 439 (M+H, 30), 347 (26), 301 (28), 255 (14), 209 (14).

RESULTS AND DISCUSSION
The nitration of TAIW in N$_2$O$_5$ enriched HNO$_3$ led to the formation of white amorphous material at first, which were low melting compound. The IR spectra of the product indicated the cleavage of the cage structure. However, after 2 h for heat preservation at 90°C, impurities were oxidized and decomposed, CL-20 can be obtained in good yield with high purity. Results are shown in Table 1.

Effect of Reaction Temperature
The pronounced effect of temperature on this reaction can be easily demonstrated from the results shown by the entries 1-4. Higher temperature is in favor of N-nitration, which also accelerates the decomposition of N$_2$O$_5$ and the increase of byproducts. The rate of nitration slows down as temperature decreases, and N$_2$O$_5$/HNO$_3$ was cumulated, which is dangerous for researchers. Experiments were carried out at 0°C, 20°C, 40°C and 60°C, yield of CL-20 was varied from 61.4% to 86.1%. Thus all the further experiments were carried out at 40°C.

Table-1: ation of TAIW using N$_2$O$_5$/HNO$_3$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temperature/°C</th>
<th>Time/h</th>
<th>n(HNO$_3$):n(N$_2$O$_5$):n(TAIW)</th>
<th>Yield/%</th>
<th>Purity/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>36:4:1</td>
<td>61.4</td>
<td>83</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>1</td>
<td>36:4:1</td>
<td>83.4</td>
<td>97</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>1</td>
<td>36:4:1</td>
<td>86.1</td>
<td>99</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>1</td>
<td>36:4:1</td>
<td>82.3</td>
<td>93</td>
</tr>
<tr>
<td>5</td>
<td>40</td>
<td>0.5</td>
<td>36:4:1</td>
<td>63.5</td>
<td>86</td>
</tr>
<tr>
<td>6</td>
<td>40</td>
<td>2</td>
<td>36:4:1</td>
<td>83.2</td>
<td>98</td>
</tr>
<tr>
<td>7</td>
<td>40</td>
<td>4</td>
<td>36:4:1</td>
<td>78.5</td>
<td>95</td>
</tr>
</tbody>
</table>
Effect of Reaction Time

To improve the performance of the system further, the effect of reaction time on yield of CL-20 was studied. Experiments were carried out at 0.5h, 1h, 2h and 4h as shown by entries 4-7. Nitration can hardly be finished completely during one hour. The yield of CL-20 increased at first and then decreased with the variety of reaction time from 0.5h to 4h. Only under the appropriate condition (1h), can the yield reach the highest (86.1%).

Effect of Molar Ratio of HNO₃, N₂O₅ and TAIW

The purpose of changing the ratio and amount of nitrating agent was to find the best synthesizing way. The pronounced effect of molar ratio of HNO₃, N₂O₅ and TAIW on this reaction can be easily demonstrated from the results shown by the entries 3, 8-13. In the experiment, we fixed the molar number of TAIW, changed the amount of N₂O₅ and HNO₃ to find the relationship among them. As the results shown, there was a significant effect on the yield when changing the molar ratio of N₂O₅. At a little higher N₂O₅ concentrations with respect to TAIW, the yield increased rapidly as the amount of N₂O₅ grew. When the amount of N₂O₅ was two times more than TAIW, more N₂O₅ even led to a lower yield. By the analysis of LC/MS, nitrating system with high N₂O₅ concentration made the ring-shaped structure cleaved. Compared with N₂O₅, the concentration of HNO₃ was less important to yield. A little increase of HNO₃ induced a higher yield. Meanwhile, nitric acid was also a solvent, too much nitric acid led to the decrease of the concentration of N₂O₅, so as to reduce the yield of CL-20.

Variation of the Crystal Formation of CL-20

Through the experiment, the crystal formation of CL-20 was found to change with the increase of the time for heat preservation. IR was one of the best methods to test the crystal formation of CL-20. As shown in Fig.1, The IR spectra was different as time went on.

![Graph showing IR spectra of CL-20 after heat preservation](image)
Mechanism of Nitration

There were four amides and two secondary amines in the cage structure of TAIW, in which secondary amine was alkaline. So, two secondary amines were firstly nitrated, then four amides are replaced by nitroamines one by one, and CL-20 was obtained at last. The reaction mechanism was as follows:

\[
\text{COCH}_3\text{CH}_3\text{CO}N\text{N N N}
\]

\[
\text{NO}2\text{CH}_3\text{CO}N\text{N N N}
\]

\[
\text{NO}2\text{COCH}_3\text{CH}_3\text{CO}
\]

Scheme-2

There were two possibilities of the nitration of acetyl group. One was the hydrolysis of acetyl group at first to form unhindered amina, and then be nitrated; the other was the directly nitrated of acetyl group. For there was sufficient $\text{N}_2\text{O}_5$ in the system, no water existed, So mechanism was proceed in the second way, which was different from the hydrolysis-nitration mechanism studied by Xiong Y J\textsuperscript{13}. According the standpoint of hydrolysis-nitration mechanism, the essence of nitration in HNO\textsubscript{3} was the combination of hydrolysis and nitration. Water was critical in the system, hydrolysis needed adequate water; meanwhile, nitration would be restricted if too much water existed. The experiment in this paper showed: the acetyl group directly replaced by nitryl group was feasible.

No water existed in the system, so there were enough concentration of NO\textsubscript{2}\textsuperscript{+}, which was a recognized nitrating agent\textsuperscript{14}. The nitrogen atom in TAIW was attacked by NO\textsubscript{2}\textsuperscript{+} to form N-cation at first, and then acetyl group with cation was dropped out. Furthermore, the nitration reaction studied here was the bimolecular electrophilic substitution, in which NO\textsubscript{2}\textsuperscript{+} attacks the lone pair on the nitrogen atom, and the cleavage of the C-N bond and the formation of the new N-N bond occur at the same time. The dependence of the reaction yield on the concentration of $\text{N}_2\text{O}_5$ seems to support the idea that the elementary reaction of the nitration was bimolecular. The nitration mechanism of TAIW in $\text{N}_2\text{O}_5$/HNO\textsubscript{3} was described as follows:

\[
\text{R C O N R}CH_3 + \text{NO}_2\xrightarrow{\text{Scheme-3}} \text{R C O N R}CH_3\text{NO}_2\]

CONCLUSIONS

A new process to synthesize CL-20 from TAIW with high yield has been developed. Various operating parameters such as reaction temperature, reaction time, and molar ratio of reagents were optimized to give maximum yield of the desired product. The crystal formation of CL-20 changed from $\alpha$-CL-20 to $\gamma$-CL-20 with the increase of the time for heat preservation. The mechanism of the reaction was also discussed. This reaction has wide scope in the nitration of a variety of other nitrogen heterocyclics. Further work is in progress to extrapolate these findings to other organic transformations.

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