CHLORIDE-ASSISTED NITROLYSIS OF CYCLIC TERTIARY AMINES

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Abstract - The synthesis of nitramines from tertiary amine heterocycles via a chloride-assisted nitrolysis is presented. The process is effective for heterocyclic systems containing a single tertiary amine moiety and gives good to excellent yields for primary, secondary and tertiary alkyl leaving groups. Heterocyclic systems containing two tertiary amines are best nitrated via a tert-butyl leaving group, with other alkyl moieties leading to ring-opened species upon treatment with nitrating media both in the presence and absence of chloride ions.

The use of chloride ions to assist in the nitration of secondary amines was extensively investigated in the middle of this century by Wright et al. Using this technique, chloride ions are oxidised to ‘electropositive’ chloride (Cl\(^+\)) by nitric acid. The electropositive chloride then converts the secondary amine to the corresponding chloramine, which is less basic than the parent amine, and finally the nitramine is formed following electrophilic attack by a nitronium ion. Typical chloride ion sources include NH\(_4\)Cl, HCl, ZnCl\(_2\) and acetyl chloride. Reaction media normally used include nitric acid/acetic anhydride mixtures in which Cl\(^+\) is stabilised as chloride acetate (ClOAc), or neat nitric acid.

Despite the success of chloride-assisted nitramine formation from secondary amines, very little work has appeared in the open literature since the late 1940’s. A recent communication from these laboratories demonstrated the advantageous use of chloride-assisted nitrolysis of a tertiary amine to form an energetic nitramine. This previously unreported route was used to form the patented nitramine 2-nitroimino-5-nitrohexahydro-1,3,5-triazine. The aim of this paper is to present a more detailed study of chloride-assisted nitramine formation. To investigate this fully, a range of alkyl leaving groups was trialed with three mono and di(tert-amine) cyclic substrates.

Previous work has shown that NH\(_4\)Cl in neat HNO\(_3\) provides optimal yields of the target nitramine. Metal chloride sources such as copper, tin and lead chloride were not used to avoid the risk of forming...
compounds possessing primary explosive properties. The tertiary amines (1a-f) were formed via a Mannich condensation of nitroguanidine, formaldehyde and the appropriate primary amine in 83-89% yield (Scheme 1).

**Scheme 1**

\[
\begin{align*}
\text{N}/\text{N}_2+\text{H}_2\text{C}=\text{O} + \text{H}_2\text{N}-\text{R} & \xrightarrow{\text{rt}-80^\circ\text{C}} 16\text{ h} \text{H}_2\text{O} \\
\text{la} & \quad \text{R} = \text{tert-butyl (87%)} \\
\text{b} & \quad \text{R} = \text{iso-propyl (89%)} \\
\text{c} & \quad \text{R} = \text{cyclohexyl (89%)} \\
\text{d} & \quad \text{R} = \text{benzyl (84%)} \\
\text{e} & \quad \text{R} = \text{n-butyl (83%)} \\
\text{f} & \quad \text{R} = \text{n-propyl (83%)} 
\end{align*}
\]

A series of comparative nitrations were carried out at 0°C to investigate the effect of various leaving groups, with all chloride-assisted reactions using 1.05 molar equivalence NH\textsubscript{4}Cl (Table 1). The previously reported tert-butyl protected species afforded the highest yield of target nitramine (2) (89%) and showed the greatest enhancement of product yield for all mono-protected species. The iso-propyl (1b) and cyclohexyl (1c) substrates gave the final nitrated species both in the presence and absence of NH\textsubscript{4}Cl. Formation of 2 from 1b and 1c in the absence of NH\textsubscript{4}Cl was unexpected and is not seen with any other alkyl leaving group. A suitable explanation for these results is not available at this stage. The use of NH\textsubscript{4}Cl in the reaction mixture, however, resulted in enhanced yields of 2 from both amines (51% and 75% respectively) and cleaner, non-exothermic reactions. The efficacy of the chloride ion was clearly demonstrated for the n-butyl and n-propyl species (1e) and (1f). Nitrolysis carried out at 0°C in neat nitric acid failed to give the target nitramine and resulted in recovery of the starting tertiary amines upon work-up. In the presence of NH\textsubscript{4}Cl, however, nitramine (2) was isolated in 59% and 68% yields from 1e and 1f respectively. The use of primary alkyl leaving groups involved longer reaction times and typically took 8 hours to complete at 0°C as opposed to 2-3 hours for secondary and tertiary alkyl moieties. Nitramine (2) was able to be isolated from 1e and 1f in neat nitric alone by allowing the reaction to proceed at 20°C, however, product yields were significantly lower. Warming to 40°C resulted in a further reduction of yield, with evidence of product decomposition by \textsuperscript{1}H NMR. Nitrolysis of the benzyl protected species (1d) resulted in benzyl decomposition products only being isolated, with no evidence of 2 or the starting amine being present.
Table 1. Effect of \( \text{NH}_4\text{Cl} \) inclusion on the synthesis of 2.

<table>
<thead>
<tr>
<th>Amine</th>
<th>( \text{Yield 2 (%), HNO}_3 )</th>
<th>( \text{Yield 2 (%) \text{NH}_4\text{Cl, HNO}_3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( 0^\circ\text{C} )</td>
<td>( 20^\circ\text{C} )</td>
</tr>
<tr>
<td>( \text{1a} )</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>( \text{1b} )</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>( \text{1c} )</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>( \text{1d} )</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>( \text{1e} )</td>
<td>0</td>
<td>28</td>
</tr>
<tr>
<td>( \text{1f} )</td>
<td>0</td>
<td>39</td>
</tr>
</tbody>
</table>

The effectiveness of chloride-assisted nitrolysis for dinitramine formation was investigated for the target 1,3,5,5-tetranitrohexahydropyrimidine (3), a patented oxidant used in explosive and rocket propellant compositions.\(^8\) Diol (4) was formed by condensation of nitromethane and formaldehyde. Ag\(^+\) induced oxidation of sodium nitrite was used to form the nitronium ion \textit{in situ} to quench the carbanion and gave 4 in 52% yield (Scheme 2).\(^9,10\)

\textbf{Scheme 2}

\[
\begin{align*}
\text{MeNO}_2 + \text{H}_2\text{C}=\text{O} & \xrightarrow{1. \text{NaOH, } 2. \text{NaNO}_2, \text{AgNO}_3} \text{4 (52\%)} \\
\text{4 (52\%)} & \xrightarrow{(\text{HCHO})_3} \text{5a-c}
\end{align*}
\]

\(5a\) \( R = \text{tert-butyl} (52\%) \\
\(5b\) \( R = \text{iso-propyl} (86\%) \\
\(5c\) \( R = \text{cyclohexyl} (93\%)

Condensation of 4 with depolymerised paraformaldehyde and primary amines (such as \textit{tert}-butylamine, \textit{iso}-propylamine and cyclohexylamine) gave the cyclic diamines (5a-c) in 52, 86 and 93% yields.
respectively. Synthesis of the n-butyl substrate was achieved using aqueous formaldehyde to give 5d in 49% yield, with the mono-butyl adduct (6) also isolated in 18% yield (Scheme 3).\(^\text{11}\)

\[ \begin{align*}
\text{Scheme 3} \\
\text{HCHO} & \xrightarrow{n\text{-BuNH}_2} \text{HCl, rt} \\
4 & \rightarrow \text{O}_2\text{N} \quad \text{NO}_2 \\
& \quad \text{Bu} \quad \text{N} \quad \text{N} \quad \text{Bu} \\
& \quad \text{O}_2\text{N} \quad \text{NO}_2 \\
& \quad \text{H} \quad \text{N} \quad \text{N} \quad \text{Bu} \\
\text{5d (49%)} & \quad + \quad \text{6 (18%)}
\end{align*} \]

Nitrolysis of tert-butyl (5a) at 0°C in neat nitric acid and 1.05 molar equivalence NH\(_4\)Cl gave the target nitramine (3) in 76% yield. Absence of the electropositive chloride species resulted in an inferior yielding reaction, with 3 isolated in 35% yield (Scheme 4).

\[ \begin{align*}
\text{Scheme 4} \\
\text{O}_2\text{N} \quad \text{NO}_2 \\
& \quad \text{tBu} \quad \text{N} \quad \text{N} \quad \text{tBu} \\
& \quad \text{O}_2\text{N} \quad \text{NO}_2 \\
\text{5a} & \rightarrow \text{3} \\
\text{i) NH}_4\text{Cl, HNO}_3 (76%)} & \quad \text{ii) HNO}_3 (35%) \\
\end{align*} \]

The dialkyl protected substrates (5b, c) failed to give 3 in nitric acid concentrations ranging from 90-100% and 1.05 molar equivalence of NH\(_4\)Cl, the products instead being the ring-opened linear nitrosamines (7a, b) (Scheme 5). The presence or otherwise of electropositive chloride had little effect on the yields of 7 obtained and failed to effect the synthesis of 3 (Table 2). Treatment of 5d under the range of conditions utilised for 5b, c above resulted in the isolation of an inseparable mixture of 7c and a second, unidentified ring-opened species. Levins et al.\(^\text{11}\) reported the formation of ring-opened compounds including 7 from 5a-d using nitric acid media at concentrations ranging from 95-100% during their attempts to form 3. The synthesis of 3 in poor yield from 5b is reported\(^\text{11}\) using 90% nitric acid, however, this reaction was unable to be reproduced in these laboratories, with 7a the only identifiable product isolated.
Table 2: Yield 7 under various nitrolysis conditions

<table>
<thead>
<tr>
<th>Amine</th>
<th>$HNO_3$, $NH_4Cl$</th>
<th>$HNO_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acid Conc (%)</td>
<td>Yield</td>
</tr>
<tr>
<td>$5b$</td>
<td>100</td>
<td>7a, 70%</td>
</tr>
<tr>
<td>$5b$</td>
<td>90</td>
<td>7a, 4%</td>
</tr>
<tr>
<td>$5c$</td>
<td>100</td>
<td>7b, 92%</td>
</tr>
<tr>
<td>$5c$</td>
<td>90</td>
<td>7b, 9%</td>
</tr>
</tbody>
</table>

Reactions carried out at 0°C for 3 hours.

Treatment of 5 with either $NH_4Cl/HNO_3$ or nitric acid (90-100%) leads to the intermediate carbocation (8), with labile groups such as tert-butyl leading ultimately to 3. Poorer leaving groups such as iso-propyl (5b), cyclohexyl (5c) and n-butyl (5d) lead instead to series (7), with none of the target nitramine (3) formed (Scheme 6).
Nitration of $5b$, $c$ was attempted using a number of nitrolysis methods including $\text{Ac}_2\text{O}/\text{HNO}_3$ and $(\text{CF}_3\text{COO})_2\text{O}/\text{HNO}_3$ in the presence and absence of $\text{NH}_4\text{Cl}$. All experiments resulted in either isolation of the ring-opened species ($7a$, $b$) or total decomposition of the ring system.

A second cyclic diamine ($9$) was synthesised in a one-pot method from nitroethane, formaldehyde and tert-butylamine in 25% yield, with the secondary amine ($10$) isolated as the major product in 55% yield (Scheme 7). Treatment of $9$ with neat nitric acid gave the mononitramine ($11$) in 50% yield. Addition of $\text{NH}_4\text{Cl}$ to the system resulted in an increase in yield to 71%. In both cases conversion to the dinitramine was unable to be achieved. Despite being structurally similar, tert-amines ($5a$) and ($9$) lead to different nitrolysis products. The fact that $5a$ undergoes two nitrolysis reactions while $9$ only participates in a single reaction can be explained on the basis of differences in basicity of the tert-butylamines. The lack of reactivity of the second amine moiety of $9$ is presumably due to protonation of the amine site, thereby preventing attack by $\text{NO}_2^+$. Previous work on the nitrolysis of $5a$ and $9$ has shown good results using $\text{H}_2\text{SO}_4/\text{HNO}_3$ and neat nitric acid respectively. Use of a chloride catalysed nitrolysis, however, allowed the reactions to proceed at either lower temperature (0°C as opposed to 45°C) or shorter reaction periods.

**Scheme 7**

\[
\text{EtNO}_2 + \text{HCHO} + \text{tBuNH}_2 \xrightarrow{\text{H}_2\text{O}, \text{rt}, 16 \text{ h}} \begin{array}{c}
\text{Me} \\
\text{N} \\
\text{N} \\
\text{tBu} \\
\end{array} + \begin{array}{c}
\text{Me} \\
\text{N} \\
\text{N} \\
\text{tBu} \\
\end{array} \\
\]

9 (25%) 10 (55%)

i) or ii)

\[
\begin{array}{c}
\text{Me} \\
\text{N} \\
\text{N} \\
\text{tBu} \\
\text{NO}_2 \\
\end{array} \\
\]

11

i) $\text{NH}_4\text{Cl}, \text{HNO}_3$ (71%)

ii) $\text{HNO}_3$ (50%)

In summary, the effectiveness of chloride-assisted nitrolysis for the formation of cyclic nitramines has been demonstrated. The process is most suitable for heterocycles containing a single tertiary amine site, with primary, secondary and tertiary alkyl leaving groups giving good to excellent yields. Nitrolysis of
heterocyclic systems containing two tertiary amine moieties have shown enhanced yields for a tert-butyl leaving group only, with all other moieties proving ineffective in the trialed substrates.

ACKNOWLEDGMENTS
The author wishes to thank Mr Mark Fitzgerald for his assistance and Dr Ian Dagley for valuable discussions.

EXPERIMENTAL SECTION
CAUTION: Compounds (2, 3, 4) and (7) are sensitive explosives and should not be subjected to impact, friction, electrostatic discharge or high temperatures. Fume cupboards rated for explosives synthesis should be used along with appropriately trained personnel. Compound (1a) was synthesised according to Cliff et al. Nmr spectra were recorded on a Varian Unity 300 Fourier Transform NMR spectrometer. $^1$H and $^{13}$C NMR spectra were measured at 300 MHz and 75.6 MHz respectively. Chemical shifts are reported as δ values in ppm and are relative to internal TMS. Melting points were determined on an Electrothermal IA 9200 melting point apparatus and are uncorrected. Low resolution MS spectra were recorded on an Electrospray Ionisation VG Quattro spectrometer with a cone voltage of 30-60 V. High resolution MS spectra were recorded on an Electrospray Ionisation VG AutoSpec with cone voltage 20-50 V, skimmer offset +10 V and a resolution of 2.5 K. All MS samples were infused in 50% MeOH/H$_2$O. Elemental analyses were performed by the National Analytical Laboratories Pty Ltd, Victoria, Australia. All samples were dried at 30°C (0.01 mmHg) for 24 h over P$_2$O$_5$ prior to elemental analysis. Spectral and analytical data is presented for previously reported compounds where literature data is inadequate.

2-Nitroimino-5-(iso-propyl)hexahydro-1, 3, 5-triazine (1b)

General Procedure
To a slurry of nitroguanidine (5.0 g, 48 mmol) in H$_2$O (20 mL) was added a 37% aqueous formaldehyde solution (8.8 mL, 82 mmol) and the mixture stirred for 30 min at rt. Iso-propylamine (3.4 g, 57.6 mmol) was then added slowly and the mixture stirred for 1 h at rt and 16 h at 80°C. The slurry was cooled to rt, filtered and the solid washed with cold water and dried to give a white powder. Recrystallisation from acetone gave the title compound as white crystalline plates (6.8 g, 89%), mp 191-192°C.

$^1$H NMR (DMSO-d$_6$) δ 8.89 (2H, s, 2xNH), 4.33 (4H, s, 2x CH$_2$), 2.88 (1H, sept, J = 6.5 Hz, CH(CH$_3$)$_2$), 1.09 (6H, d, J = 6.3 Hz, 2x CH$_3$); $^{13}$C NMR (DMSO-d$_6$) δ 156.1 (C=N), 57.8 (2xCH$_2$), 47.3 (CH), 20.8 (2xCH$_3$); IR (KBr) 3330, 3204, 3123, 2976, 1588 (NO$_2$), 1462, 1304 cm$^{-1}$; MS (ES+ve) m/z 188 (M+H$^+$).
5-Cyclohexyl-2-nitroiminohexahydro-1, 3, 5-triazine (1c)

Using the general procedure described above for the synthesis of 1b with a reaction time of 72 h at ambient temperature, the title compound was obtained as a white powder (89%) after recrystallisation from acetone, mp 190-191°C.

$^1$H NMR (DMSO-$d_6$) δ 8.85 (2H, s, 2xNH), 4.35 (4H, s, 2xCH$_2$), 2.59-2.50 (1H, m, CH), 1.90-1.54 (4H, m, 2xCH$_2$), 23.5 (CH$_2$), 24.5 (2xCH$_2$); IR (KBr) 3343, 3312, 3200, 2925, 2853, 1593 (NO$_2$), 1474, 1382, 1299, 1248, 1108 cm$^{-1}$; MS (ES+ve) m/z 228 (M+H$^+$, 100), 183 (19); Anal. Calcd for C$_6$H$_{13}$NsO$_2$: C, 38.50; H, 7.00; N, 34.41. Found: C, 38.89; H, 7.36; N, 37.70.

5-Benzyl-2-nitroiminohexahydro-1, 3, 5-triazine (1d)

Using the general procedure described above for the synthesis of 1b with a reaction time of 72 h at ambient temperature, the title compound was obtained as white, crystalline needles (84%) after recrystallisation from acetone, mp 217-218°C.

$^1$H NMR (DMSO-$d_6$) δ 8.77 (2H, s, 2xNH), 7.43-7.28 (5H, m, 5xAr-H), 4.24 (4H, s, 2xCH$_2$), 3.79 (2H, s, CH$_2$Ph); $^{13}$C NMR (DMSO-$d_6$) δ 155.5 (C=N), 137.4 (Ar-C1), 128.7 (Ar-C3, 5), 128.3 (Ar-C1, 6), 127.4 (Ar-C4), 59.3 (2xCH$_2$), 53.7 (CH$_2$Ph); IR (KBr) 3356, 3194, 3120, 2359 (w), 1594 (NO$_2$), 1481, 1310, 1244, 1109 cm$^{-1}$; MS (ES+ve) m/z 236 (M+H$^+$, 100), 191 (19); Anal. Calcd for C$_{16}$H$_{17}$NsO$_2$: C, 51.06; H, 5.57; N, 29.77. Found: C, 50.72; H, 5.29; N, 29.64.

5-Butyl-2-nitroiminohexahydro-1, 3, 5-triazine (1e)

Using the general procedure described above for the synthesis of 1b with a reaction time of 72 h at ambient temperature, the title compound was obtained as white, crystalline needles (83%) after recrystallisation from acetone, mp 181-183°C.

$^1$H NMR (DMSO-$d_6$) δ 8.68 (2H, s, 2xNH), 4.24 (4H, s, 2xCH$_2$), 2.56 (2H, t, $J = 7.2$ Hz, NCH$_2$), 1.46-1.26 (4H, m, CH$_2$CH$_2$), 0.89 (3H, t, $J = 7.2$ Hz, CH$_3$); $^{13}$C NMR (DMSO-$d_6$) δ 155.6 (C=N), 59.7 (2xCH$_2$), 49.2 (NCH$_2$), 29.3 (CH$_2$CH$_2$CH$_2$), 19.6 (CH$_2$CH$_3$), 13.8 (CH$_3$); IR (KBr) 3349, 3203, 3124, 2929, 1601, 1313, 1104 cm$^{-1}$; MS (ES+ve) m/z 202 (M+H$^+$, 100), 186 (M-CH$_3^+$, 6), 157 (23); Anal. Calcd for C$_7$H$_{15}$NsO$_2$: C, 41.78; H, 7.51; N, 34.80. Found: C, 41.90; H, 7.80; N, 34.90.
2-Nitroimino-5-propylhexahydro-1, 3, 5-triazine (1f)

Using the general procedure described above for the synthesis of 1b, the title compound was obtained as white, crystalline needles (83%) after recrystallisation from acetone, mp 196-198°C.

$^1$H NMR (DMSO- $d_6$) $\delta$ 8.89 (2H, s, 2xNH), 4.24 (4H, s, 2xCH$_2$), 2.55-2.51 (2H, m, NCH$_2$), 2.55-2.51 (2H, m, CH$_2$CH$_3$), 0.88 (3H, t, $J$ = 7.1 Hz, CH$_3$); $^{13}$C NMR (DMSO- $d_6$) $\delta$ 156.0 (C=N), 59.7 (2xCH$_2$), 51.5 (NCH$_2$), 20.4 (CH$_2$CH$_3$), 11.4 (CH$_3$); IR (KBr) 3339, 3203, 3126, 2956, 1613 (NO$_2$), 1348, 1319, 1238, 1107 cm$^{-1}$; MS (ES+ve) m/z 188 (M+H$^+$, 100), 172 (M-CH$_3^+$, 11), 143 (53); Anal. Calcd for C$_9$H$_{13}$N$_5$O$_2$: C, 38.50; H, 7.00; N, 37.41. Found: C, 38.56; H, 6.60; N, 37.77.

5-Nitro-2-nitroiminohexahydro-1, 3, 5-triazine (2)

General Nitration Procedure for Amines 1b, c, e, f.

To 100% nitric acid (3.0 mL) at 0°C was added amine (1b) (500 mg, 2.67 mmol) over a 10 min period. Ammonium chloride (150 mg, 2.80 mmol) was then added and the resulting yellow solution was stirred at 0°C for 3 h and poured onto ice (10 g). The precipitated solid was stirred for 1 h at rt until the aqueous phase became clear and then chilled to 0°C, filtered, washed with cold water and dried in vacuo to give pure 2 as a white solid (260 mg, 51%), mp 205-206°C. Spectral data was consistent with that previously reported by Cliff et al.$^4$

1, 3, 5, 5-Tetranitrohexahydropyrimidine (3)

To neat nitric acid (4.0 mL) at 0°C was added the cyclic amine (5a) (400 mg, 1.39 mmol) over a 10 min period. Ammonium chloride (78 mg, 1.46 mmol) was then added and the resulting solution was stirred at 0°C for 2 h and then poured onto ice (7 g). The precipitated solid was filtered, washed with cold water and dried in vacuo to give pure 3 as a white solid (280 mg, 76%), mp 150-151°C.

$^1$H NMR (acetone- $d_6$) $\delta$ 6.31 (2H, s, NCH$_2$N), 5.47 (4H, s, 2xCH$_2$); $^{13}$C NMR (acetone- $d_6$) $\delta$ 107.7 (C(NO$_2$)$_2$), 60.0 (NCH$_2$N), 49.7 (2xCH$_2$); IR (KBr) 3034, 1576 (NO$_2$), 1547 (NO$_2$), 1380, 1295, 994, 894 cm$^{-1}$; MS (ES+ve) m/z 250 (M-O$^+$, 4), 219 (M-NO$_2^+$, 16), 174 (20), 159 (100); HRMS calcd for C$_9$H$_6$N$_6$O$_7$ 250.0298, found 250.0299.

2, 2-Dinitro-1, 3-propanediol (4)

The title compound was synthesised by the procedure of Borgardt et al.$^{10}$ Recrystallisation from ether/CH$_2$Cl$_2$ gave the diol as a light yellow solid (52%), mp 134-135°C.
1H NMR (CDCl$_3$) δ 4.57 (4H, s, 2xCH$_2$), 2.60 (2H, s(b), 2xOH); 13C NMR (DMSO-d$_6$) δ 119.1 (C(NO$_2$)$_2$), 60.1 (2 x CH$_2$); IR (KBr) 3280 (OH), 1587, 1569 (N=O), 1350, 1320, 1069 cm$^{-1}$; MS (ES+ve) m/z 135 (M-CH$_2$OH$^+$, 100), 105 (19), 59 (10).

1, 3-Di(tert-butyl)-5, 5-dinitrohexahydropyrimidine (5a)

**General Procedure**

To a solution of 4 (5.50 g, 33.1 mmol) in methanol (6 mL) at 0°C was slowly added tert-butylamine (4.76 g, 65.2 mmol) in methanol (6 mL). The ice bath was removed and the mixture was allowed to stir at rt for 30 min then cooled to 0°C and a methanolic solution of depolymerised paraformaldehyde added (effected by refluxing paraformaldehyde (1.15 g, 36 mmol) and potassium carbonate (4 mg) in absolute methanol (10 mL) for 24 h). The reaction was warmed to rt for 30 min and then heated to reflux for 4 h. The solution was chilled to 0°C for 24 h and the resulting solid was collected and washed with cold methanol to give the title compound as an off-white crystalline solid (4.85 g, 52%), mp 77-78°C.

1H NMR (acetone-d$_6$) δ 3.69 (4H, s, 2xCH$_2$), 3.61 (ZH, s, NCH$_2$N), 1.14 (10xH, d, J = 6.6 Hz, 2xCH); 13C NMR (acetone-d$_6$) δ 116.0 (C(NO$_2$)$_2$), 63.9 (2xCH$_2$), 54.5 (NCH$_2$N), 51.6 (2xCH(CH$_3$)$_3$), 69.3 (2xCH); IR (KBr) 2973, 1564 (NO$_2$), 1366, 1206, 1036 cm$^{-1}$; MS (ES+ve) m/z 289 (M+H$^+$, 100), 244 (8), 171 (39); HRMS calcd for C$_{13}$H$_{25}$N$_4$O$_4$ 289.1876, found 289.1863.

1, 3-Di(iso-propyl)-5, 5-dinitrohexahydropyrimidine (5b)

Using the general procedure described above for the synthesis of 5a, the title compound was obtained as a yellow oil (86%) after purification by column chromatography (4% ethyl acetate/hexane).

1H NMR (CDC$_3$) δ 3.58 (4H, s, 2xCH$_2$), 3.46 (2H, s, NCH$_2$N), 2.97 (2H, sept, J = 6.6 Hz, 2xCH), 1.09 (2x6H, d, J = 6.6 Hz, 2xCH(CH$_3$)$_2$); 13C NMR (CDC$_3$) δ 113.4 (C(NO$_2$)$_2$), 69.3 (NCH$_2$N), 52.4 (2xNCH$_2$), 51.3 (2xCH), 18.4 (4 x CH$_3$); IR (neat) 2968, 1580 (NO$_2$), 1463, 1322, 1238, 1103 cm$^{-1}$; MS (EI+ve) m/z 259 (M-H$^+$, 13), 213 (M-HNO$_2^+$, 10), 196 (24), 183 (35), 157 (20), 114 (100); HRMS calcd for C$_{10}$H$_{19}$N$_4$O$_4$ 259.1407, found 259.1404.

1, 3-Dicyclohexyl-5, 5-dinitrohexahydropyrimidine (5c)

Using the general procedure described above for the synthesis of 5a, the title compound was obtained as a yellow oil (93%) after purification by column chromatography (10% ethyl acetate/hexane). The oil solidified on standing to give a light yellow solid, mp 81-82°C.

1H NMR (CDC$_3$) δ 3.62 (4H, s, 2xCH$_2$), 3.54 (2H, s, NCH$_2$N), 2.54-2.47 (2H, m, 2xCH), 1.84-1.10 (20H, m, 10xCH$_2$); 13C NMR (CDC$_3$) δ 113.5 (C(NO$_2$)$_2$), 69.1 (NCH$_2$N), 61.2 (2 x NCH$_2$), 52.3 (2xCH),
29.1 (4xCH₂), 25.9 (2xCH₂), 25.5 (4xCH₂); IR (KBr) 2935, 2848, 1576 (NO₂), 1440, 1098 cm⁻¹; MS (EI+ve) m/z 339 (M-H⁺, 39), 294 (M-NO₂⁺, 22), 276 (32), 247 (10), 141 (18), 112 (18); HRMS calcd for C₇H₁₇N₄O₃ 339.2033, found 339.2032.

1,3-Dibutyl-5,5-dinitrohexahydropyrimidine (5d) and 1-butyl-5,5-dinitroheptahydropyrimidine (6)
The title compounds were synthesised by the procedure of Levins et al.¹¹ Purification by column chromatography (5% ethyl acetate/hexane) gave 5d as a light orange oil (49%) and 6 as a light yellow oil (18%).

5d ¹H NMR (CDCl₃) δ 3.66 (4H, s, 2xCH₂), 3.40 (2H, s, NCH₂N), 2.53 (2x2H, t, J = 7.3 Hz, 2xNCH₂), 1.55-1.22 (2x4H, m, 2xCH₂CH₂), 0.92 (2x3H, t, J = 7.2 Hz, 2xCH₃); ¹³C NMR (CDCl₃) δ 112.4 (C(NO₂)₂), 73.2 (NCH₂N), 55.8 (2xCH₂), 53.7 (2xCH₂), 29.0 (2xNCH₂CH₂), 20.2 (2xCH₂CH₃), 13.9 (2xCH₃); IR (neat) 2958, 2932, 2870, 1576 (NO₂), 1466, 1320, 1211, 1100 cm⁻¹; MS (EI+ve) m/z 287 (M-H⁺, 21), 242 (M-NO₂⁺, 100); HRMS calcd for C₁₂H₂₄N₃O₂ 242.1869, found 242.1869.

6 ¹H NMR (CDCl₃) δ 4.62 (2H, s, CH₂), 4.41 (2H, s, CH₂), 4.03 (2H, s, CH₂), 2.63 (2H, t, J = 7.2 Hz, CH₂CH₂), 1.48-1.24 (4H, m, CH₂CH₂), 0.90 (3H, t, J = 7.0, CH₃); ¹³C NMR (CDCl₃) δ 109.4 (C(NO₂)₂), 83.6 (NCH₂N), 69.1 (CH₂), 54.2 (CH₂), 51.2 (CH₂), 29.7 (NCH₂CH₂), 19.9 (CH₂CH₃), 13.8 (CH₃); IR (neat) 2959, 2871, 1576 (NO₂), 1444, 1350, 1317, 1209 cm⁻¹; MS (EI+ve) m/z 233 (M+H⁺, 8), 190 (100), 144 (38), 98 (38).

N, N'-Di(iso-propyl)-N-nitro-N'-nitroso-2,2-dinitropropyl-1, 3-diamine (7a)

General Procedure
To neat HNO₃ (4.0 mL) at 0°C was added iso-propylamine 5b (300 mg, 1.15 mmol) in a single addition. Solid NH₄Cl (65 mg, 1.21 mmol) was added and the resulting yellow solution was stirred for 3 h at 0°C. The solution was poured onto ice (6 g), filtered and the solid was washed with cold water and dried to give the title compound as a white powder (260 mg, 70%), mp 106-108°C (explosive decomp.).

¹H NMR (CDCl₃) δ 4.71 (2H, s, CH₂), 4.61 (2H, s, CH₂), 4.57-4.37 (2H, m, 2xCH), 1.60 (6H, d, J = 6.7 Hz, CH(CH₃)₂), 1.39 (6H, d, J = 6.8 Hz, CH(CH₃)₂); ¹³C NMR (CDCl₃) δ 116.4 (C(NO₂)₂), 57.9 (CH₂), 57.2 (CH₂), 51.8 (CH), 46.2 (CH), 22.3 (2xCH₃), 18.9 (2x CH₃); IR (KBr) 3009, 2977, 2940, 1584, 1567, 1546, 1468, 1384, 1280 cm⁻¹; MS (EI+ve) m/z 322 (M⁺, 5), 280 (39), 143 (56), 127 (39); HRMS calcd for C₉H₁₈N₆O₇ 322.1236, found 322.1231.
N, N'-Dicyclohexyl-N-nitro-N'-nitroso-2,2-dinitropropyl-1,3-diamine (7b)

Using the general procedure described above for the synthesis of 7a, the title compound was obtained as a white solid (92%), mp 136°C (explosive decamp.).

\[^1\text{H NMR} \quad (\text{acetone-d}_6) \delta 5.02 \ (2\text{H}, \text{s}, \text{CH}_2), 4.87 \ (2\text{H}, \text{s}, \text{CH}_2), 4.34-4.12 \ (2\text{H}, \text{m}, \text{2xCH}), 2.26-1.21 \ (20\text{H}, \text{m}, \text{2x(CH)ds}; \text{I}3c \ \text{NMR} \quad (\text{acetone-d}_6, \text{In part}) \delta 65.8 \ (\text{CH}_2), 64.9 \ (\text{CH}_2), 53.0 \ (\text{CH}), 47.3 \ (\text{CH}), 33.6 \ (2 \times \text{CH}_2), 26.2 \ (2 \ x \text{CH}_2), 26.1 \ (2 \ x \text{CH}_2), 25.7 \ (\text{CH}_2), 25.5 \ (\text{CH}_2); \text{IR} \quad (\text{KBr}) 2932, 2856, 1534, 1571, 1560, 1425, 1282, 1080 \ \text{cm}^{-1}; \text{MS} \quad (\text{LSIMS}) \ m/z 403 \ (\text{M}+\text{H}^+, \text{18}), 373 \ (\text{11}), 183 \ (76), 107 \ (34), 83 \ (100); \text{HRMS} \quad \text{calcd for} \quad \text{C}_{13}\text{H}_{27}\text{N}_6\text{O}_7 \quad 403.1942, \text{found 403.1955}.

1,3-Di(tert-butyl)-3-methyl-3-nitrohexahydropyrimidine (9) and 1-(tert-butyl)-3-methyl-3-nitroheptahydropyrimidine (10)

To a solution of nitroethane (3.0 g, 40 mmol) in MeOH (20 mL) at 0°C was slowly added an aqueous solution of 36% formaldehyde (8.0 mL) followed by tert-butylamine (2.78 g, 38 mmol). The mixture was warmed to rt and stirred for 16 h before cooling to 0°C. The precipitated solid was collected by filtration, dried and purified by column chromatography (10% ethyl acetate/hexane) to give 9 (1.20 g, 25%, mp 115-116°C) and 10 (2.06 g, 55%, mp 79-80°C) as white, crystalline solids.

\[^1\text{H NMR} \quad (\text{CDCl}_3) \delta 3.87 \ (1\text{H}, \text{d}, \text{J} = 8.3 \text{ Hz}), 3.64 \ (2\text{H}, \text{d}, \text{J} = 11.8 \text{ Hz}), 2.91 \ (1\text{H}, \text{d}, \text{J} = 8.3 \text{ Hz}), 2.35 \ (2\text{H}, \text{d}, \text{J} = 11.7 \text{ Hz}), 1.50 \ (3\text{H}, \text{s}, \text{CH}_3), 1.10 \ (9\text{H}, \text{s}, \text{C(CH)ds}); \text{I}3c \ \text{NMR} \quad (\text{CDCl}_3) \delta 85.6 \ (\text{C(CH)NO}) , 63.9, 53.5, 27.5, 26.3 \ (\text{C(CH)ds}), 24.1; \text{IR} \quad (\text{KBr}) 2971, 2874, 2825, 2751, 2751, 2702, 1540 \ (\text{NO}) , 1450, 1348, 1212, 1048 \ \text{cm}^{-1}; \text{MS} \quad (\text{ES+ve}) \ m/z 258 \ (\text{M}+\text{H}^+, \text{100}); \text{HRMS} \quad \text{calcd for} \quad \text{C}_{13}\text{H}_{28}\text{N}_3\text{O}_2 \quad 258.2182, \text{found} \quad 258.2177.

\[^1\text{H NMR} \quad (\text{CDCl}_3) \delta 4.60 \ (2\text{H}, \text{dt}, \text{J} = 2.0, 7.6 \text{ Hz}), 3.95 \ (1\text{H}, \text{d}, \text{J} = 7.9 \text{ Hz}), 3.82 \ (1\text{H}, \text{dt}, \text{J} = 2.0, 12.3 \text{ Hz}), 3.47 \ (1\text{H}, \text{d}, \text{J} = 12.4 \text{ Hz}), 2.59 \ (1\text{H}, \text{d}, \text{J} = 12/3 \text{ Hz}), 1.46 \ (3\text{H}, \text{s}, \text{CH}_3), 1.09 \ (9\text{H}, \text{s}, \text{C(CH)ds}); \text{I}3c \ \text{NMR} \quad (\text{CDCl}_3) \delta 84.5, 81.2, 71.5, 53.1, 52.7, 26.5, 21.6; \text{IR} \quad (\text{KBr}) 2974, 2877, 2824, 2774, 1540 \ (\text{NO}) , 1470, 1349, 1235, 1168, 1087, 1028 \ \text{cm}^{-1}; \text{MS} \quad (\text{ES+ve}) \ m/z 203 \ (\text{M}+2\text{H}^+, \text{100}), 191 (8\%), 147 (37\%).

1-(tert-Butyl)-3-methyl-3,5-dinitrohexahydropyrimidine (11)

To 98% HNO\(_3\) (4.0 mL) at 0°C was added NH\(_2\)Cl (66 mg 1.22 mmol) and the resulting solution stirred for 5 min. Amine (9) (250 mg, 0.97 mmol) was added slowly over a 10 min period and the mixture stirred at 0°C for 2 h. The mixture was then poured onto ice (8 g) and the resulting precipitate collected to give the title compound as a white solid (170 mg, 71%), mp 115-116°C.

\[^1\text{H NMR} \quad (\text{acetone-d}_6) \delta 5.53 \ (1\text{H}, \text{dt}, \text{J} = 1.6, 11.7 \text{ Hz}), 5.40 \ (1\text{H}, \text{dt}, \text{J} = 1.6, 15.1 \text{ Hz}), 4.15 \ (1\text{H}, \text{d}, \text{J} = 11.8 \text{ Hz}), 3.95 \ (1\text{H}, \text{dt}, \text{J} = 1.9, 12.9 \text{ Hz}), 3.86 \ (1\text{H}, \text{d}, \text{J} = 15.2 \text{ Hz}), 1.66 \ (3\text{H}, \text{s}, \text{CH}_3), 1.21 (9\text{H}, \text{s},
C(CH$_3$)$_3$; $^{13}$C NMR (acetone-$d_6$) δ 86.2, 63.8, 54.3, 52.6, 26.3, 25.5, 22.6; IR (KBr) 2977, 2542, 1556 (b), 1384 (b), 1183, 1013, 881 cm$^{-1}$; MS (ES+ve) m/z 247 (M+H$^+$, 100), 200 (M-NO$_2^+$, 9), 191 (46); HRMS calcd for C$_9$H$_9$N$_4$O$_4$ 247.1406, found 247.1405.

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