ANIONIC [3,3] REARRANGEMENTS OF CYCLIC HYDRAZINE DIACYCLATES TO MEDIUM-SIZE CYCLIC DIAMIDES AND THEIR STRUCTURES.

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Abstract- The anionic rearrangement of N,N'-dimethyl-N,N'-diacylhydrazines to 1,2-disubstituted succinamides proceeds in the presence of a adjacent enolate-stabilizing substituent such as a phenyl group. However, a substituent that poorly stabilizes the α-carbanion results in an extremely low yield of the products. The [3,3] sigmatropic rearrangement generally requires a chair form for the cyclic six-centered transition state. When the dienolates of N,N'-diacylhydrazines have favorable steric factors for the cyclic transition state, the rearrangement seems to proceed smoothly. The diacylates of 5- to 8-membered cyclic hydrazine which readily adopt a favorable conformation for the [3,3] rearrangement readily rearrange to 9- to 12-membered cyclic diamides.

The 3,4-diaza [3,3] sigmatropic rearrangement is important in the fields of synthetic and mechanistic organic chemistry. An example of the aromatic version of the rearrangement is the first step in the conversion of N-aryl-N'-enylhydrazines to indoles. We previously reported an aliphatic version of anionic rearrangements of N,N'-diacylhydrazines and N-acyl-N'-enylhydrazines. The C-C bond-forming rearrangement can be rationalized in terms of hetero [3,3] sigmatropic shifts of dienolated precursors. These investigations indicated that the carboxamide enolate can be employed as a component of [3,3] rearrangement precursors. When the dienolates of N,N'-diacylhydrazines are stable enough to form the cyclic six-centered structure required in the [3,3] sigmatropic shifts transition state, the rearrangement proceeds smoothly to give 1,2-disubstituted succinamides in up to 50 % yield. However, the rearrangement of N,N'-diacylhydrazines without a substituent stabilizing the adjacent enolate, such as a phenyl group does not proceed effectively. When the enolates are not stable enough to proceed the rearrangement, restriction to a favorable conformational state for the cyclic transition state can be employed to advantage in the rearrangements. For example, in the case of similar [3,3] rearrangement of N,O-diacylhydroxylamines, a bulky substituent on the nitrogen was effective for the C-C bond-forming rearrangement. N,O-Diacyl-N-tert-butylhydroxylamine rearranged to the succinic acid
derivatives in 68% yield, although the substrate does not have an α-stabilizing group.\textsuperscript{6} However, introduction of a tert-butyl group on the nitrogen of the \textit{N,N'}-diacylhydrazines did not improve the result. In this paper, we wish to report the [3,3] rearrangement of diacylates of cyclic hydrazines which are conformationally restricted to a favorable conformation for the rearrangement in terms of methylene linkage to give cyclic diamides.

The 5- to 8-membered cyclic hydrazines (tetrahydropyrazole, hexahydropyridazine, hexahydro-1,2-diazepine, octahydro-1,2-diazocine) were prepared as reported,\textsuperscript{7} and were readily converted into \textit{N,N'}-diacyl cyclic hydrazines. Treatment of \textit{N,N'}-diacetyl-5- and 6-membered cyclic hydrazines (1\textsuperscript{a} (n= 3) and 1\textsuperscript{b} (n= 4)) with 5.0 eq of lithium diisopropylamide (LDA) in THF at -78°C, then 20°C for 2 h and 50°C for 15 h did not give the expected cyclic diamides (2\textsuperscript{a} and 2\textsuperscript{b}). In contrast, \textit{N,N'}-diacetyl-7- and 8-membered cyclic hydrazines (1\textsuperscript{c} (n= 5) and 1\textsuperscript{d} (n= 6)) rearranged under the same conditions to 11- and 12-membered cyclic diamides (2\textsuperscript{c} and 2\textsuperscript{d}) in low yields.\textsuperscript{8} Although a rate-acceleration effect of a dimethyl substituent on the reaction sites of the [3,3] rearrangement was reported,\textsuperscript{9} acyclic \textit{N,N'}-isobutyryl-\textit{N,N'}-dimethylhydrazine did not give the [3,3] rearranged product.\textsuperscript{10} \textit{N,N'}-Diisobutyryl 5- to 8-membered cyclic hydrazines (1\textsuperscript{e}-1\textsuperscript{h} (n= 3- 6)) rearranged upon treatment with 5.0 eq of LDA in THF at 20°C for 2 h to afford 9- to 12-membered cyclic diamides (2\textsuperscript{e}-2\textsuperscript{h}) in 5-79% yields.

\begin{center}
\includegraphics[width=\textwidth]{fig1.png}
\end{center}

Table 1. [3,3] Rearrangement of \textit{N,N'}-Diacyl Cyclic Hydrazines

<table>
<thead>
<tr>
<th>Compound</th>
<th>n</th>
<th>R</th>
<th>Yield (%) of Cyclic Diamide\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>3</td>
<td>H</td>
<td>0</td>
</tr>
<tr>
<td>b</td>
<td>4</td>
<td>H</td>
<td>0</td>
</tr>
<tr>
<td>c</td>
<td>5</td>
<td>H</td>
<td>13</td>
</tr>
<tr>
<td>d</td>
<td>6</td>
<td>H</td>
<td>12</td>
</tr>
<tr>
<td>e</td>
<td>3</td>
<td>CH\textsubscript{3}</td>
<td>5</td>
</tr>
<tr>
<td>f</td>
<td>4</td>
<td>CH\textsubscript{3}</td>
<td>62</td>
</tr>
<tr>
<td>g</td>
<td>5</td>
<td>CH\textsubscript{3}</td>
<td>79</td>
</tr>
<tr>
<td>h</td>
<td>6</td>
<td>CH\textsubscript{3}</td>
<td>20</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Yields are isolated yields. All starting materials were enolized with 5.0 eq of LDA at -78°C in THF and the temperature was allowed to rise from -78°C to 20°C over 30 min. It was held at 20°C for 2 h, then raised to 50°C for 5 h for 1\textsuperscript{a}-1\textsuperscript{d}; it was just held at 20°C for 2 h for 1\textsuperscript{e}-1\textsuperscript{h}.

Rearrangements of \textit{N,N'}-diacyl cyclic hydrazines with a phenyl group stabilizing the α-carbanion proceed smoothly, compared with the acyclic case.\textsuperscript{4} \textit{N,N'}-Diphenylacetyl 5- to 8-membered cyclic hydrazines,
(3a-3d (n= 3- 6)) also rearranged upon treatment with 3.0 eq of LDA in THF at 20°C for 2 h, then at 50°C for 3.5 h to give the 9- to 12-membered cyclic diamides (4 and 5) in 66-91% yields. Although the conformation of 5- and 8-membered cyclic hydrazides are not favorable for the rearrangement (Table 1), stabilization effect by phenyl group seems to compensate the disadvantage.

![Chemical structures](image)

Table 2. [3,3] Rearrangement of N,N'-Diacyl Cyclic Hydrazines with a Phenyl Group

<table>
<thead>
<tr>
<th>Compound</th>
<th>n</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>dl : meso</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>3</td>
<td>66</td>
<td>0 : 100</td>
</tr>
<tr>
<td>b</td>
<td>4</td>
<td>74</td>
<td>83 : 17</td>
</tr>
<tr>
<td>c</td>
<td>5</td>
<td>91</td>
<td>92 : 8</td>
</tr>
<tr>
<td>d</td>
<td>6</td>
<td>87</td>
<td>45 : 55</td>
</tr>
</tbody>
</table>

<sup>a</sup> Yields are isolated yields. All starting materials were enolized with 3.0 eq of LDA at -78°C in THF and the temperature was allowed to rise from -78°C to 20°C over 30 min, then held at 20°C for 2 h and raised to 50°C for 3.5 h.

![Figure 1](image)

Figure 1. ORTEP drawing of the 9-membered (5a, left) and 10-membered diamides (4b, right)

The reaction of N,N'-diphenylacetyltetrahydropyrazole (3a) gave the 9-membered compound (5a) as the sole product. The <sup>1</sup>H-NMR spectrum of 5a indicates that the conformational structure lacks symmetry,
and is distinct from those of the other cyclic products (4b-4d, 5b-5d). The structure of 5a was determined by X-Ray crystallography. The crystal of 5a belongs to triclinic space group P1, with cell constant \( a = 9.475(1), b = 10.382(2), c = 9.271(1) \), \( Z = 2 \), and the final \( R \)-value was 0.056. The ORTEP drawing of the structure of 5a is shown in Figure 1. Unexpectedly, both of the amide bonds of 5a were trans in spite of the strain in the 9-membered ring system.

In the rearrangements of 3b-3d, the dl-products (4b-4d) and the meso-products (5b-5d) are formed. Their \(^1\)H-NMR spectra showed similar tendencies for the two isomers and indicate that the conformational states have symmetry. If both of the isomers have symmetrical conformation, the dl-product has C2 symmetry, and the meso product has a symmetrical plane. From these results and examination of molecular models, the structures of the isomers were deduced. Our conclusion was confirmed by an X-Ray study on 4b, the crystal of which belongs to monoclinic space group Cc, with cell constant \( a = 17.47(2), b = 10.468(4), c = 9.707(4) \), \( Z = 4 \), and the final \( R \)-value was 0.100. The ORTEP drawing of the structure of 4b is shown in Figure 2. The stereochemistry of the rearranged products depends on the ring size of the cyclic hydrazine. Because of the relatively high temperature and strongly basic condition, the dl:meso ratios of products are assumed to reflect the thermodynamic stability.

Conformational analyses of simple lactams have been conducted by using several kinds of measurements.\(^{11}\) These studies clearly indicate that 5- to 8-membered lactams have the cis conformation and 10-membered and larger lactams have the trans conformation. The 9-membered lactam, azacyclononanone, exists as an equilibrium mixture of cis and trans conformers, the relative amounts of which depend on the solvent.\(^{12}\) The cis- and trans- structures and interconversion of amide bonds play important roles in specifying the conformational behavior of peptides as well as low-molecular-weight biologically active substances. For example, we have reported that tumor-promoting teleocidins, which have a 9-membered lactam structure including an indole ring, exist in an equilibrium of two conformational states in solution owing to cis-trans isomerization.\(^{13}\) We have also reported the determination of the active conformation of teleocidins by the design and synthesis of conformationally restricted teleocidin mimics, benzolactams, which have an 8-membered lactam structure including a benzene ring.\(^{14}\) On the other hand, conformational structures of medium-size cyclic diamides have been investigated in connection with partial structures of peptides. An 8-membered cyclic diamide, 1,5-diazaoctane-2,6-dione, exists as a two cis amide structure.\(^{15}\) A 10-membered cyclic diamide, 1,6-diazacyclodecane-2,7-dione, exists as a two trans amide structure in solution and in the crystalline state.\(^{16}\) In the present study, we found that a 9-membered cyclic diamide, cis-7,8-diphenyl-1,5-diazacyclononane-6,9-dione (5a) and a 10-membered cyclic diamide, trans-3,4-diphenyl-1,6-diazacyclononane-2,5-dione (4b) have two trans amides in the crystalline state. The present synthetic method for cyclic diamides employing anionic [3,3] rearrangement should be useful for the preparation of 9- to 12-membered cyclic diamides and for further investigation of conformational behaviors and transannular interactions in these compounds.
EXPERIMENTAL

General Remarks. Melting points were obtained on a Yanagimoto micro hot stage without correction. 1H-NMR spectra were recorded with a JEOL JMN-FX-400 spectrometer (400 MHz), with tetramethylsilane (TMS) as an internal standard and chemical shifts are given in ppm as δ values from TMS. MS spectra were recorded on a JEOL JMS-D-300 for DI-MS. Column chromatography was performed on silica gel (Merck 7734 or 9385 (flash chromatography)).

N,N'-Diacyl Cyclic Hydrazine (1 and 3); Typical Procedure for N,N'-Diphenylacetyltetrahydro-pyrazole (3a) A solution of phenylacetyl chloride (1.39 g, 9.0 mmol) in THF (3 mL) was added dropwise to a stirred solution of tetrahydropyrazole hydrochloride (326 mg, 3.0 mmol) and K2CO3 (912 mg, 2.2 mmol) in THF-H2O (1:1, 10 mL) at rt. The mixture was stirred for 10 h, then sat. NaHCO3 aqueous solution (30 mL) was added to it, and the mixture was extracted with ethyl acetate (4 x 50 mL). The organic layer was washed with brine (50 mL), dried (MgSO4), filtered and concentrated. The product was purified by silica gel column chromatography using CH2Cl2/ethyl acetate as the eluent to give 3a (795 mg, 86%). Spectral data of the products are as follows.

1a: colorless syrup, 1H-NMR (CDCl3) 2.05 (m, 2H), 2.15 (s, 6H), 2.97 (m, 2H), 4.32 (m, 2H); HR-MS Calcd for C7H12N2O2: 156.0899. Found: 156.0893.
1b: mp 57-59°C (ether/n-hexane), 1H-NMR (CDCl3) 1.71 (m, 4H), 2.09 (m, 6H), 2.70 (m, 2H), 4.63 (m, 2H); Anal. Calcd for C8H14N2O2: C, 56.45, H, 8.29, N, 16.46. Found: C, 56.16, H, 8.47, N, 16.40.
1c: mp 65-66°C (ether/hexane), 1H-NMR (CDCl3) 1.53 (m, 2H), 1.70 (m, 2H), 1.84 (m, 2H), 2.03 (s, 6H), 3.06 (m, 2H), 4.27 (m, 2H); Anal. Calcd for C9H16N2O2: C, 58.67, H, 8.75, N, 15.20. Found: C, 58.97, H, 8.57, N, 15.50.
1d: mp 43°C (ether/n-hexane/ethyl acetate), 1H-NMR (CDCl3) 1.11 (d, 12H, J = 6.6 Hz), 1.70 (m, 4H), 2.71 (m, 2H), 2.94 (m, 2H), 4.68 (m, 2H); HR-MS Calcd for C10H18N2O2: 198.1368. Found: 198.1384.
1e: pale brown syrup, 1H-NMR (CDCl3) 1.11-1.22 (m, 12H), 2.77 (m, 2H), 3.04 (m, 2H), 4.34 (m, 2H); Anal. Calcd for C13H24N2O2: C, 64.96, H, 10.07, N, 11.66. Found: C, 64.91, H, 9.83, N, 11.89.
1f: colorless syrup, 1H-NMR (CDCl3) 1.11 (d, 12H, J = 6.6 Hz), 1.70 (m, 4H), 2.71 (m, 2H), 2.94 (m, 2H), 4.68 (m, 2H); HR-MS Calcd for C12H22N2O2: 226.1681. Found: 226.1687.
1g: mp 53-54°C (n-hexane), 1H-NMR (CDCl3) 1.11-1.13 (m, 12H), 1.57 (m, 2H), 1.68 (m, 2H), 1.83 (m, 2H), 2.77 (m, 2H), 3.04 (m, 2H), 4.34 (m, 2H); Anal. Calcd for C14H26N2O2: C, 64.96, H, 10.07, N, 11.66. Found: C, 64.91, H, 9.83, N, 11.89.
1h: mp 64-65°C (CH2Cl2/n-hexane), 1H-NMR (CDCl3) 1.03-1.16 (m, 12H), 1.42-1.75 (m, 6H), 2.63 (m, 1H), 2.79 (m, 1H), 3.01 (m, 1H), 3.35 (m, 1H), 4.00 (m, 1H), 4.35 (m, 1H); HR-MS Calcd for C14H26N2O2: 254.1994. Found: 254.2001.
3a: mp 78-79°C (ethyl acetate), 1H-NMR (CDCl3) 1.80 (m, 2H), 2.50 (m, 2H), 3.59 (d, 2H, J = 14.7Hz), 3.67 (d, 2H, J = 14.7Hz), 4.15 (m, 2H), 7.22-7.52 (m, 10H); HR-MS Calcd for C15H20N2O2: 308.1525. Found: 308.1523.
3b: mp 118-120°C (CH2Cl2/n-hexane), 1H-NMR (CDCl3) 1.57 (m, 4H), 2.36 (m, 2H), 3.45 (d, 2H, J = 14.3 Hz), 3.53 (d, 2H, J = 14.3 Hz), 4.52 (m, 2H), 7.20-7.34 (m, 10H); Anal. Calcd for C20H22N2O2: C, 74.50, H, 6.88, N, 8.69. Found: C, 74.32, H, 6.73, N, 8.97.
Rearrangements of 1 and 3: General Procedure: A solution of freshly distilled diisopropylamine (0.70 mL, 5.0 mmol for 1a-1h, 0.42 mL, 3.0 mmol for 3a-3d) in THF (3 mL) was treated with 1.6 M n-BuLi in hexane (3.12 mL, 5.0 mmol for 1a-1h, 1.87 mL, 3.0 mmol for 3a-3d) at -20 °C under Ar. After having been stirred for 15 min at 0°C, the LDA solution was cooled to -78°C, and a solution of 1 (2 mmol) in THF (4 mL) was added at -78°C with stirring. The reaction mixture required an additional 30 min for the temperature to rise from -78°C to 20°C. It was held at 20°C for 2 h, then raised to 50°C for 1.5 h for 1a-1d, to 50°C for 3.5 h for 3a-3d, or not raised for 1e-1h. Stirring was continued during the periods described above, then the reaction was quenched by the addition of saturated NH₄Cl aqueous solution (5 mL). The mixture was diluted with brine (30 mL) and extracted with ethyl acetate (4 x 100 mL). The organic layer was washed with 5% HCl (80 mL), saturated NaHCO₃ aqueous solution (80 mL) and brine (80 mL), dried over MgSO₄, filtered and concentrated. The residue was crystallized from CH₂Cl₂/n-hexane to give a major product. The filtrate was concentrated and chromatographed on silica gel using CH₂Cl₂/ethyl acetate to give the rearranged C-C products (2) from 1, and (4) and (5) from 3. Spectral data of the products are as follows.

2c: colorless amorphous powder, ¹H-NMR (DMSO-d₆, 70°C) 1.41 (m, 6H), 2.27 (s, 4H), 3.15 (m, 4H), 7.36 (br s, 2H); HR-MS Calcd for C₉H₁₆N₂O₂: 184.1212. Found: 184.1210.

2d: colorless amorphous powder, ¹H-NMR (DMSO-d₆, 70°C) 1.25 (m, 4H), 1.46 (m, 4H), 2.29 (s, 4H), 3.15 (m, 4H), 7.29 (br s, 2H); HR-MS Calcd for C₁₀H₁₈N₂O₂: 198.1368. Found: 198.1396.

2e: colorless amorphous powder, ¹H-NMR (DMSO-d₆, 70°C) 1.01 (s, 12H), 1.67 (m, 2H), 2.84 (m, 2H), 3.52 (m, 2H), 6.31 (br s, 2H); HR-MS Calcd for C₁₁H₂₀N₂O₂: 212.1525. Found: 212.1521.

2f: mp 178-180°C (ethyl acetate), ¹H-NMR (DMSO-d₆, 70°C) 1.12 (s, 12H), 1.55 (m, 4H), 2.97 (m, 4H), 6.83 (br s, 2H); Anal. Calcd for C₁₂H₂₂N₂O₂: C, 63.68, H, 9.80, N, 12.38. Found: C, 63.81, H, 9.65, N, 12.34.

2g: mp 184-186°C (ethyl acetate/n-hexane), ¹H-NMR (DMSO-d₆, 70°C) 1.14 (s, 12H), 1.43 (m, 2H), 1.50 (m, 4H), 3.11 (m, 4H), 6.82 (br s, 2H); Anal. Calcd for C₁₃H₂₄N₂O₂: C, 64.96, H, 10.07, N, 11.66. Found: C, 64.66, H, 10.09, N, 11.46.

2h: mp 185-187°C (ethyl acetate), ¹H-NMR (DMSO-d₆, 70°C) 1.18 (s, 12H), 1.25 (m, 4H), 1.50 (m, 4H), 3.18 (m, 4H), 6.62 (br s, 2H); Anal. Calcd for C₁₄H₂₆N₂O₂: C, 66.10, H, 10.30, N, 11.01. Found: C, 66.13, H, 10.17, N, 11.07.

5a: mp 177-180°C (ethyl acetate), ¹H-NMR (DMSO-d₆, 70°C) 1.78 (m, 2H), 2.92 (m, 2H), 3.56 (m, 1H), 3.73 (m, 1H), 4.30 (d, 1H, J = 7.7 Hz), 4.40 (d, 1H, J = 7.7 Hz), 5.79 (m, 1H), 7.04-7.34 (m, 6H), 7.37 (d, 2H, J = 7.0 Hz), 7.52 (m, 1H), 7.65 (d, 2H, J = 7.0 Hz); Anal. Calcd for C₁₉H₂₆N₂O₂: C, 74.06, H, 6.54, N, 9.08. Found: C, 74.11, H, 6.67, N, 9.08.
4b: mp 176-177°C (ethyl acetate), 1H-NMR (DMSO-d$_6$, 70°C) 1.65 (m, 4H), 2.94 (m, 2H), 3.20 (m, 2H), 4.36 (s, 2H), 7.07 (t, 2H, $J = 7.3$ Hz), 7.13 (t, 4H, $J = 7.3$ Hz), 7.25 (br s, 1H), 7.47 (d, 4H, $J = 7.3$ Hz); Anal. Calcd for C$_{20}$H$_{22}$N$_2$O$_2$: C, 74.50, H, 6.88, N, 8.69. Found: C, 74.49, H, 6.93, N, 8.81.

5b: mp 136-138°C (ethanol), 1H-NMR (DMSO-d$_6$, 70°C) 1.51 (m, 2H), 1.79 (m, 2H), 2.60 (m, 2H), 3.39 (m, 2H), 4.20 (s, 2H), 7.05 (t, 2H, $J = 7.3$ Hz), 7.13 (t, 4H, $J = 7.3$ Hz), 7.28 (d, 2H, $J = 7.3$ Hz), 7.95 (br s, 1H); Anal. Calcd for C$_{20}$H$_{22}$N$_2$O$_2$: C, 74.50, H, 6.88, N, 8.69. Found: C, 74.39, H, 6.93, N, 8.76.

4c: mp 224-227°C (ethyl acetate), 1H-NMR (DMSO-d$_6$, 70°C) 1.38 (m, 2H), 1.51 (m, 2H), 1.65 (m, 2H), 2.64 (m, 2H), 3.62 (m, 2H), 4.25 (s, 2H), 7.09-7.15 (m, 6H), 7.21 (br s, 1H), 7.41 (dd, 4H, $J = 2.5, 8.1$ Hz); Anal. Calcd for C$_{21}$H$_{24}$N$_2$O$_2$: C, 74.97, H, 7.19, N, 8.33. Found: C, 74.76, H, 7.04, N, 8.41.

5c: not isolated, 1H-NMR (DMSO-d$_6$, 70°C) 1.51 (m, 6H), 3.11 (m, 2H), 3.33 (m, 2H), 4.31 (s, 2H), 7.01 (t, 2H, $J = 7.3$ Hz), 7.03-7.43 (m, 8H), 7.88 (m, 1H).

4d: mp >300°C (ethyl acetate), 1H-NMR (DMSO-d$_6$, 70°C) 1.35-1.70 (m, 8H), 3.11 (m, 2H), 3.35 (m, 2H), 4.29 (s, 2H), 7.07-7.28 (m, 8H), 7.31 (dd, 4H, $J = 1.8, 7.3$ Hz); Anal. Calcd for C$_{22}$H$_{26}$N$_2$O$_2$: C, 75.39, H, 7.48, N, 7.99. Found: C, 75.26, H, 7.66, N, 8.19.

5d: mp >300°C (ethanol), 1H-NMR (DMSO-d$_6$, 70°C) 1.08 (m, 2H), 1.47 (m, 2H), 1.63 (m, 4H), 2.64 (m, 2H), 4.32 (s, 2H), 7.01 (t, 2H, $J = 7.3$ Hz), 7.08 (t, 4H, $J = 7.3$ Hz), 7.27 (d, 2H, $J = 7.3$ Hz), 7.87 (d, 2H, $J = 8.8$ Hz); Anal. Calcd for C$_{22}$H$_{26}$N$_2$: C, 75.39, H, 7.48, N, 7.99. Found: C, 75.45, H, 7.74, N, 8.11.

REFERENCES AND NOTES
1. This numbering system for hetero analogs of [3,3] sigmatropic rearrangements has been employed by R. P. Lutz, Chem Rev., 1984, 84, 205.
8. The acyclic $N,N'$-diacetyl-$N,N'$-dimethylhydrazine gave no C-C rearrangement product under these conditions.