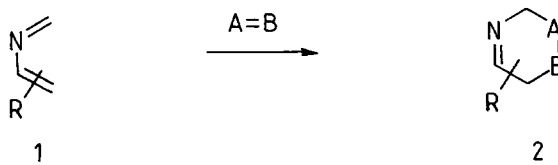


1,4-DEHYDROCHLORINATION OF  $\alpha$ -CHLOROIMINES AS A SUITABLE PROCEDURE  
FOR THE SYNTHESIS OF UNACTIVATED 2-AZA-1,3-DIENES AND  
3-AZA-1,3,5-TRIENES

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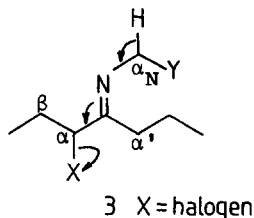
**Abstract** : N-Benzyl and N-allyl  $\alpha$ -chloroimines were dehydrochlorinated in a 1,4-fashion to afford the corresponding 2-aza-1,3-dienes and 3-aza-1,3,5-trienes, respectively.

2-Aza-1,3-dienes 1 have become valuable building blocks for the construction of heterocyclic compounds 2 by cycloaddition with dienophiles.<sup>1-7</sup> The powerful cycloaddition capacity of 2-aza-1,3-dienes was also demonstrated recently in an intramolecular version.<sup>8</sup> The applicability and exploration of the chemistry of 2-azadienes is dependent upon the availability of synthetic methods for the preparation of these compounds. Important entries



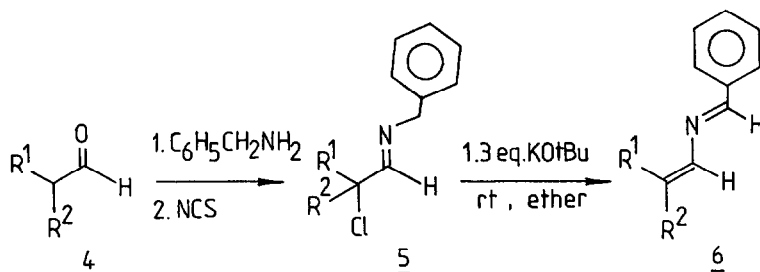
hitherto entail the base-catalyzed isomerization of N-allyl imines<sup>9-11</sup> and N-benzyl  $\alpha,\beta$ -unsaturated imines,<sup>12</sup> coupling of N-(phosphonomethyl)imines,<sup>13,14</sup> N-[bis(trimethylsilyl)methyl]imines,<sup>15</sup> N-(triphenylsilyl)methylimines<sup>13</sup> or N,N-bis(trimethylsilyl)enamines<sup>16</sup> with ketones or aldehydes, and fluoride induced protodesilylation of N-(1-triethylsilylallyl)imines.<sup>17</sup> Some of these routes are relatively general syntheses but very often they utilize difficultly accessible starting materials. In the present paper, an elegant entry into 2-aza-1,3-dienes starting from easily accessible  $\alpha$ -chloroimines 5 is disclosed. The  $\alpha$ -haloimino system 3 contains several deprotonation sites, including the  $\alpha$ -position (usually the fastest deprotonated, but it does not lead to any end product), the  $\alpha'$ -position (leading to the Favorskii rearrangement),<sup>18</sup> the  $\beta$ -position (affording  $\alpha,\beta$ -unsaturated imines

upon 1,2-dehydrohalogenation)<sup>19</sup> and the  $\alpha_N$ -position, provided substituent Y is an activating group enhancing the acidity of the  $\alpha_N$ -hydrogens. The lat-



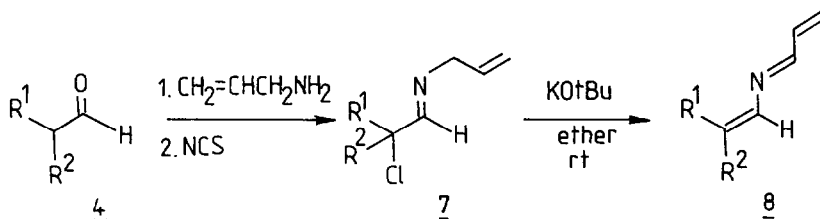
ter deprotonation of  $\alpha$ -haloimines is used as a basis for the 1,4-elimination of hydrogen halide (see the set of arrows in 3).<sup>20</sup>

The reaction of N-(2-chloro-1-alkylidene)benzylamines 5, easily obtai-



ned from imination of aldehydes and subsequent  $\alpha$ -chlorination, with potassium t-butoxide in ether at room temperature furnished 2-aza-1,3-dienes 6 in good yields (Table). Compounds 6 were fully characterized by spectrometric methods (<sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, MS).

In similar way, N-(2-chloro-1-alkylidene)allylamines 7 were transformed into



3-aza-1,3,5-trienes 8 by a base-induced 1,4-dehydrochlorination using potassium t-butoxide (Table). The azatrienes 8 are rather labile and should be kept under an inert atmosphere at low temperature (-20°C) or should be used immediately in further reactions.<sup>21</sup>

While 1,2-dehydrochlorination of N-(arylidene)-2-chloroethylamine is known to give 1-aryl-2-aza-1,3-dienes,<sup>22</sup> the analogous reaction of N-(2-me-

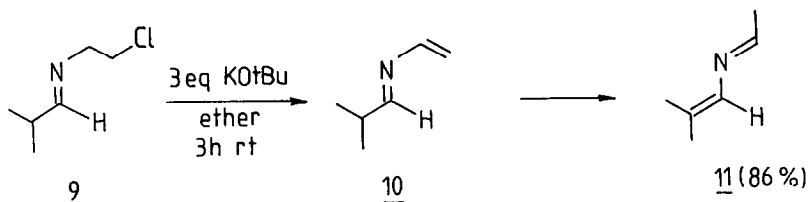
Table : Synthesis of 2-Aza-1,3-dienes 6 and 3-Aza-1,3,5-trienes 8 from  $\alpha$ -Chloroimines

$\alpha$ -Chloro-imine	R <sup>1</sup>	R <sup>2</sup>	Reaction Time <sup>a</sup>	Yield of <u>6</u> or <u>8</u>	Bp °C/mmHg
<u>5a</u>	Me	Me	5h	<u>6a</u> : 91% <sup>a</sup>	80-83/0.5 <sup>b</sup>
<u>5b</u>	Et	Et	16h	<u>6b</u> : 88%	68-71/0.1
<u>5c</u>	(CH <sub>2</sub> ) <sub>5</sub>		19h	<u>6c</u> : 72%	97-100/0.3
<u>7a</u>	Me	Me	17h	<u>8a</u> : 83%	72-75/56
<u>7b</u>	Et	Et	16h	<u>8b</u> : 76%	39-44/0.4
<u>7c</u>	(CH <sub>2</sub> ) <sub>5</sub>		15h	<u>8c</u> : 84%	47-49/0.4

<sup>a</sup> Reaction conditions : the substrates 5 or 7 (10% w/v) and 1.3 equiv. KOt-Bu in dry ether are stirred at room temperature.

<sup>b</sup> Lit.<sup>9</sup> bp. 72°C/1.5 mmHg.

thyl-1-propylidene)-2-chloroethylamine 9 with potassium t-butoxide in ether at room temperature provided 2-aza-1,3-diene 11 in which the conjugated double bond shifted toward the more substituted system. Compound 11 decom-



poses rapidly upon standing at ambient temperature. This labile 2-azadiene was obtained as a crude oily product with a purity of about 95%. Any attempt to purify this material resulted in less pure product.

In conclusion, the 1,4-dehydrochlorination of  $\alpha$ -chloroimines provides an elegant entry into unactivated 2-aza-1,3-dienes and 3-aza-1,3,5-trienes.

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