Direct Imination of Chalcones with Aminimide: Formation of Aziridines

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Because of the strong nucleophilicity of a divalent nitrogen atom and the presence of a good leaving group, aminimides can be regarded as useful ylids in organic synthesis.

Using the aminimide, prepared from 1,1-dimethylhydrazine and oxirane\(^1\), we recently reported the one-step conversion of aldehydes into nitriles under mild reaction conditions in good yields\(^2\). Appel et al. have prepared trimethylaminimide and investigated the reactions of this aminimide with electrophiles, including two imination reactions\(^3\). Attempts to prepare a three-membered ring compound, one of the two imination reactions, was reported to result in the formation of a diaziridine from a Schiff base (C\(_5\)H\(_5\)-CH=CH-N-C\(_4\)H\(_5\),c) in 1.8% yield. In the course of further studies on the reactions of aminimides with electrophiles, we expected the aminimides to react at an activated carbon-carbon double bond rather than at the double bond of the Schiff bases to give the aziridine derivatives. As shown in the Scheme, the aminimide 1 may attack the \(\beta\)-carbon atom of the chalcone 2, followed by cyclization to the aziridine 4 with release of dimethyl-(2-hydroxypropyl)amine which is easily soluble in water.

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{N-H}_2 \quad + \quad \text{H}_3\text{C} \\
\text{H}_2\text{N} & \quad \text{OH} \quad \xrightarrow{\text{C}_2\text{H}_5\text{OH}, 50^\circ\text{C}, 3h} \\
\text{CH}_3 & \quad \text{OH} \\
\text{HN-N} & \quad \text{CH}_2-\text{CH}-\text{CH}_3 \\
& \quad \text{CH}_3
\end{align*}
\]

The synthesis of such aziridines 4 was previously achieved\(^4\) by indirect imination of chalcones, involving at least the two steps, halogenation and amination, leading to cyclization to give the aziridine. There is a report concerning a direct imination of chalcone with free sulfilimine\(^5\). This ylid, however, required several steps to prepare, a long reaction time in the further imination reaction, and complicated techniques were necessary in the work-up process.

The present, aminimide method, is a facile, one-pot reaction. This method has simplicity in the synthesis of the ylid, the imination reaction procedure, and the work-up process. Several chalcones 2a-d were converted to aziridines by the
3-Benzoyl-2-phenylaziridine (4a):
A mixture of dimethylhydrazine (0.3 g, 5 mmol), methylxirane (0.45 g, 7.7 mmol), and 2-propanol (5 ml) is heated at 50°C for 3 h in a tightly stoppered vessel. Chalcone (2a; 0.85 g, 4.1 mmol) dissolved in a mixture of 2-propanol (12 ml) and benzene (3 ml) is then added dropwise into the ammimide solution obtained with stirring at 50°C. After stirring for 4 h, the solvent is removed with a rotary evaporator. The residue is extracted with ether. Recrystallization from methanol gives 3-benzoyl-2-phenylaziridine (4a) as needles; yield: 0.68 g (74%); m.p. 99-101°C.

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Table. Aziridines 4a-d

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield</th>
<th>m.p. [°C]</th>
<th>Molecular formula* or Lit. m.p. [°C]</th>
<th>l.R. (KBr)</th>
<th>ν [cm⁻¹]</th>
<th>¹H-N.M.R. (CDCl₃) δ [ppm]</th>
<th>M.S. m/e ( % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>74</td>
<td>99-101°</td>
<td>C₇H₈N₂ClO</td>
<td>3240, 1665</td>
<td>2.68 (t, NH, J = 8 Hz); 3.16 (dd, H-C-2, J = 8, 2.4 Hz); 3.48 (dd, H-C-3, J = 8, 2.4 Hz) 223</td>
<td></td>
<td></td>
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<tr>
<td>4b</td>
<td>89</td>
<td>75-78°</td>
<td>C₇H₈ClN</td>
<td>3300, 1665</td>
<td>2.60 (b, NH); 3.12 (bs, H-C-2)³; 3.40 (bs, H-C-3)⁵</td>
<td>257</td>
<td></td>
</tr>
<tr>
<td>4c</td>
<td>81</td>
<td>142-144°</td>
<td>C₅H₆ClN</td>
<td>3300, 1665</td>
<td>2.76 (t, NH, J = 8 Hz); 3.25 (dd, H-C-2, J = 8, 2.4 Hz); 3.50 (dd, H-C-3, J = 8, 2.4 Hz) 268</td>
<td></td>
<td></td>
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<tr>
<td>4d</td>
<td>67</td>
<td>92.5-94.5°</td>
<td>C₅H₆ClN</td>
<td>3240, 1670</td>
<td>2.60 (t, NH, J = 8 Hz); 3.36 (dd, H-C-2, J = 8, 2.4 Hz); 3.43 (dd, H-C-3, J = 8, 2.4 Hz) 257</td>
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</table>

* The microanalyses were in satisfactory agreement with the calculated values (C ±0.3, H ±0.3).
* Addition of D₂O resulted in a doublet, J = 2.5 Hz.

The present method. The results are given in the Table. The products obtained were identified by l.R., ¹H-N.M.R., and mass spectra and m.p. The configuration of these aziridines is proved to be trans from the coupling constant between the methine protons in ¹H-N.M.R. spectra (J = 2-3 Hz)³.

2-Hydroxychalcone, however, on similar treatment with the amminide did not give the expected aziridine, instead the starting chalcone was recovered quantitatively after acidification of the reaction mixture. Even when an excess amminide (2 mol to chalcone) was employed the result is the same as above. The salt 5,

which must be formed immediately in the reaction mixture, does not react with the amminide, whereas salicylaldehyde was converted easily to the nitrile by amminide 1 under the same conditions. The difference in these reactivities may show that the phenolate anion blocks the β-position rather than the carbonyl carbon.