Note

Synthesis of 2-nitroimino-1,3-diazacycloalkanes

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An efficient, practical and enviro-friendly method of preparation of 2-nitroimino-1,3-diazacycloalkanes 3a-d has been reported by a simple reaction between nitroguanidine 1 and diamines 2a-d in the presence of conc. HCl in aq. medium with very good yields.

2-Nitroimino-1,3-diazacycloalkanes are important compounds in the synthesis of medicinal compounds, pesticides, insecticides, and nematicides. Further, 2-nitroimino-1,3-diazacycloalkanes is a very important intermediate in the preparation of imidacloprid, which is a present day pesticide used worldwide. There are some procedures reported for the preparation of 2-nitroimino-1,3-diazacycloalkanes. The general method for the preparation of diazacycloalkanes is the reaction between nitroguanidine and diaminedihydrochloride in the presence of base like potassium hydroxide. Very old method of making these diazacycloalkanes is the reaction between diamine and cyanogen bromide. Another report describes the preparation of these diazacycloalkanes, by heating of thiopeudourea and diamine in aqueous solution. Because of certain limitations associated with the above methods, there exists a scope to develop a practical method for the preparation of these cycloalkanes.

Our continuing interest in the preparation of pesticides, have led us to report an efficient, practical and enviro-friendly method for the preparation of 2-nitroimino-1,3-diazacycloalkanes 3a-d (Scheme 1).

Nitroguanidine10 and aliphatic diamines 2a-d were taken in water and heated to desirable temperature with catalytic amount of conc. hydrochloric acid and the product was filtered off in very good yields (Table 1). The products are characterized by their spectral data. The aqueous filtrate was recycled to conduct the same reaction. The ammonia evolved during the reaction was controlled by proper stirring and it could be trapped to make liquor ammonia. The recycling of aqueous filtrate of the reaction makes the method enviro-friendly, unlike the other procedures where sulphur product methane thiol was emitted and potassium chloride was formed. The cyanogen bromide method has limitation because of handling of cyanogen bromide and the bromide product formed.

The present reaction was found to be ineffective under these conditions when various aromatic 1,2-diamines like 1,2-phenylenediamine, 4-bromo-1,2-phenylenediamine and 4-methyl-1,2-phenylenediamine were employed. In conclusion, the method reported has the advantages such as mild reaction conditions, simple work-up, enviro-safety and has the practical applicability.

<table>
<thead>
<tr>
<th>Compd</th>
<th>Amine</th>
<th>Temp. °C</th>
<th>Time (hr)</th>
<th>mp °C</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>1,2-Diaminoethane</td>
<td>56</td>
<td>8</td>
<td>220</td>
<td>76</td>
</tr>
<tr>
<td>3b</td>
<td>1,3-Diaminopropane</td>
<td>56</td>
<td>8</td>
<td>226</td>
<td>64</td>
</tr>
<tr>
<td>3c</td>
<td>1,4-Diaminobutane</td>
<td>56</td>
<td>8</td>
<td>199</td>
<td>64</td>
</tr>
<tr>
<td>3d</td>
<td>1,6-Diaminohexane</td>
<td>80</td>
<td>10</td>
<td>193</td>
<td>58</td>
</tr>
</tbody>
</table>

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Experimental Section

General. Melting points were obtained on a Toshniwal melting point apparatus and are uncorrected. IR spectra were recorded on a Nicolet 740 FT-IR spectrometer. 1H NMR spectra on a Gemini 200 MHz spectrometer in CDCl3 and DMSO-d6, with TMS as internal standard and mass spectra on a VG Micro Mass 7070H.

2-Nitroimino-1,3-diazacyclopentane 3a: Ethylenediamine (2a, 19g; 0.317 mole) was added to a stirred solution of nitroguanidine (1, 33g, 0.317 mole) in water (190g) and conc. hydrochloric acid (25mL) at room temperature over a period of 15 min. The contents were heated to 56°C for 8 hr. During the reaction copious amounts of ammonia gas evolved and there was a change in the consistency of mass. Then the heating stopped and the reaction mass was cooled to 0°C. The solid was filtered, washed with cold water and dried to give 2-nitroimino-1,3-diazacyclopentane (3a, 31.3g; 76% yield) as a solid.

Micro Mass room temperature over a period of 15 min. The contents were heated to 56°C for 8 hr. During the reaction copious amounts of ammonia gas evolved and there was a change in the consistency of mass. Then the heating stopped and the reaction mass was cooled to 0°C. The solid was filtered, washed with cold water and dried to give 2-nitroimino-1,3-diazacyclopentane (3a, 31.3g; 76% yield) as a solid.

Anal. Calcd for C27H14N3O2: C, 45.16; H, 7.52; N, 30.1. Found: C, 45.29; H, 7.56; N, 30.14%.

Acknowledgement

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References and Notes
10. Nitroguanidine was prepared in 94% yield according to our modified method of organic syntheses Davis T L, Org Synth Coll Vol 1, 1948, 399.