One-Pot Synthesis of Hexatriynediamines

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Hexatriynediamines 4 are conveniently prepared by successive treatment of 5,6,6-trichloro-5-hexen-1,3-diylnamines 1 with butyllithium, cyanogen bromide and a secondary aliphatic amine.

By combining the perchlorobutenyne of Roedig² with the lithium aminoethynides of Ficini,³ the preparation of 5,6,6-trichloro-5-hexene-1,3-diylnamines 1 can be performed in fairly good yields.⁴ In analogy with our synthesis of butadiyne diamines⁵ via 3,4,4-trichloro-3-buten-1-ynylamines we attempted the conversion of 1 into the corresponding novel hexatriynediamines 4. The reaction was carried out by treating 1 with two equivalents of butyllithium, followed by successive addition of cyanogen bromide, and two equivalents of a secondary aliphatic amine, to furnish the desired hexatriynediamines 4 in a convenient one-pot procedure. Although none of the intermediates was isolated, it is plausible to suppose that 1 is first dehalogenated to give the lithium aminohexatriynide 2, which is then brominated by cyanogen bromide to yield 3, and that finally the bromine of 3 is substituted by nucleophilic attack of the amine.

It should be noted that representatives of 4 with two different dialkylamino groups can, in general, be synthesized by two different modes: either one of the dialkylamino groups can be present at the beginning (see 1), while the other is introduced by nucleophilic substitution of the bromine (see 3 → 4). The diethylamino morpholino compound has been synthesized in both ways (see 4f and 4f, respectively).

The hexatriynediamines 4 thus obtained are relatively stable and can be stored without decomposition for some weeks in a refrigerator (0–5°C). The structure of the novel triynediamines 4 is confirmed by satisfactory microanalyses, by intensive IR absorptions in the C=C region, by very simple proton-NMR spectra and especially by the characteristic ¹³C-NMR spectra: six singlets appear in the region of acetylenic carbons (δ = 53–87 ppm) in the spectra of both unsymmetrically substituted derivatives 4a and 4d, while in the case of the bis(morpholino) compound only three signals are observed in the same region.

IR and ¹H-NMR spectra were recorded on a Perkin-Elmer 394 infrared spectrophotometer and on a Varian EM 390 spectrometer, respectively. The described ¹³C-NMR spectra of 4a, c and d were recorded at 50.28 MHz with a Bruker WP 200 spectrometer. Microanalyses were performed by using a CHN Analyzer Model 240 from Perkin-Elmer. The melting points (dec.) were determined with an automatic apparatus. Modell FP 5 from Mettler, and visually controlled in a copper block.

Hexatriynediamines 4: General Procedure:

To a well stirred solution of 4-butylnitrene in hexane (70 ml, 1.6 molar, 112 mmol) first the same volume of anhydrous ether (70 ml) and then a solution of 1a–e (50 mmol) in anhydrous ether (200 ml) are added dropwise at −70°C. The resulting mixture (containing 2) is allowed to warm to −10°C over 2–3 h and is then recooled to −70°C. A solution of cyanogen bromide (5.61 g, 33 mmol) in ether (75 ml) is added dropwise. The resulting solution containing 3 is allowed to warm again to −10°C over 2 h, is then recooled to −70°C and slowly treated with a solution of a secondary aliphatic amine HNR²R² (100 mmol) in ether (50 ml). The reaction mixture is allowed to warm to room temperature over 2 h and is then stirred overnight. The mixture is then poured on ice/water (~500 ml). The organic layer is washed with water (100 ml), dried with anhydrous calcium chloride, treated with charcoal,
<table>
<thead>
<tr>
<th>Product</th>
<th>Yield (%)</th>
<th>m.p. (°C)</th>
<th>Molecular Formula</th>
<th>IR ν (cm⁻¹)</th>
<th>¹H-NMR (CDCl₃/TMS)</th>
<th>¹³C-NMR (CDCl₃/TMS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>47</td>
<td>124–125</td>
<td>C₁₂H₁₉N₂O₂</td>
<td>2190 vs</td>
<td>3.10 (m, 4H, NCH₂); 3.28 (s, 3H, NMe); 3.67 (m, 4H, OCH₂); 6.75–7.45 (m, 5H)</td>
<td>86.11, 79.81, 69.86, 67.68, 59.20, 54.01 (6 s, acetylenic-C), 39.30 (q), 51.45 (t), 66.68 (t), 114.97 (d), 122.05, 129.47 (3d), 143.91 (s)</td>
</tr>
<tr>
<td>b</td>
<td>64</td>
<td>114–115</td>
<td>C₁₄H₁₈N₂</td>
<td>2190 vs</td>
<td>1.57 (m, 6H, 3CH₃); 3.15 (m, 4H, NCH₂); 3.31 (s, 3H, NMe); 6.8–7.4 (m, 5H)</td>
<td>–</td>
</tr>
<tr>
<td>c</td>
<td>53</td>
<td>13–155</td>
<td>C₁₄H₁₈N₂O₂</td>
<td>2190 s</td>
<td>3.13 (m, 8H, NCH₂); 3.67 (m, 8H, OCH₂)</td>
<td>85.24, 67.93, 53.95 (3s; acetylenic-C); 66.07 (t), 51.4b (t)</td>
</tr>
<tr>
<td>d</td>
<td>26</td>
<td>125–126</td>
<td>C₁₄H₁₈N₂O₂</td>
<td>2190 v</td>
<td>1.57 (m, 6H, 3CH₃); 3.15 (m, 8H, NCH₂); 3.72 (m, 4H, OCH₂)</td>
<td>86.84, 84.95, 68.20, 67.68, 53.81, 53.32 (6 s; acetylenic-C), 65.81 (t), 51.39 (t), 52.50 (t), 24.96 (t), 23.33 (t)</td>
</tr>
<tr>
<td>e</td>
<td>15</td>
<td>124–125</td>
<td>C₁₄H₁₈N₂O₂</td>
<td>2170 vs</td>
<td>1.66–1.96 (m, 4H); 3.0–3.4 (m, 8H, NCH₂); 3.6–3.8 (m, 4H, OCH₂)</td>
<td>–</td>
</tr>
<tr>
<td>f/f'</td>
<td>22/15</td>
<td>55–56</td>
<td>C₁₄H₁₈N₂O₂</td>
<td>2180 vs</td>
<td>1.18 (t, 6H, J = 7 Hz, NCH₂CH₃); 3.00 (q, 4H, J = 7 Hz, NCH₂CH₃); 3.12 (m, 4H, NCH₂); 3.70 (m, 4H, OCH₂)</td>
<td>–</td>
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</tbody>
</table>

* Decomposition.

Satisfactory microanalyses obtained: C ± 0.27, H ± 0.18, N ± 0.18, except for 4a (C – 0.45).

filtered and concentrated under reduced pressure. Solvent is added. (see Table 1) followed by cooling to afford the crude products 4, which are recrystallized from the same solvent or solvent mixture.

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