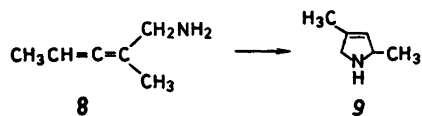
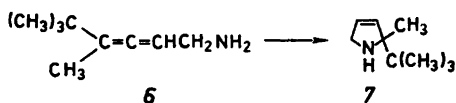
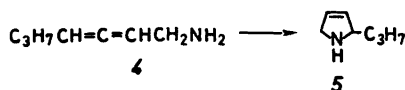
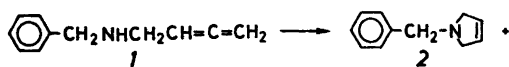


Allenes and Acetylenes. XVIII.* Synthesis of 3-Pyrrolines by Silver(I)- catalyzed Cyclization of Allenic Amines

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While purifying the allenic amine **1** by GLC (Carbowax 20 M, stainless steel column, 210 °C) we observed its complete decomposition into two new compounds formed in roughly equal amounts. These could be isolated and NMR evidence suggested that they might have structures **2** and **3**. The formation of the pyrrole **3** can be rationalized by assuming fast dehydrogenation (in the injector port) of the first formed 3-pyrroline (**2**). The isolated compound **2**, in line with this reasoning, gave large amounts of compound **3** upon reinjection into the GLC instrument.



The amine **1** is perfectly stable to normal distillation conditions (< 120 °C) and it seemed reasonable to assume that the cyclization might be metal-catalyzed. We therefore tested the behaviour of **1** towards silver tetrafluoroborate, a reagent which is a powerful catalyst in some reactions of acetylenes with cyclic transition states, e.g. the isomerisation of propargylic

acetates to 1,2-alkadienyl acetates.² This reagent (ca. 0.05 equiv) in chloroform did lead to complete cyclization of compound **1** to the 3-pyrroline **2** within 5 h at room temperature. The pyrrole **3** was not formed in amounts detectable by ¹H NMR (< 3 %). The primary amines **4** and **6** underwent equally ready cyclizations to the new 3-pyrrolines **5** and **7**, respectively.

Previous synthetic methods for 3-pyrrolines³ are not as generally applicable to the synthesis of compounds with widely different substitution patterns as is the present one. Since allenic primary and secondary amines are readily available from the corresponding alcohols,⁴ or by other methods^{1,4} the present synthetic procedure should be valuable in preparations of the relatively rare 3-pyrrolines and possibly of substituted pyrrolidines.

In addition to the above results, we have noticed ready cyclization of the differently substituted amine **8**¹ when it was subjected to GLC purification. The resulting pyrroline **9** was isolated and characterized by NMR.

Experimental. For general description see Ref. 5. The ¹H NMR spectra (60 MHz) were recorded in CDCl₃ solution. The preparations of the starting allenic amines will be described elsewhere.⁶

General procedure for cyclizations of the allenic amines, N-benzyl-2,3-butadienamine (1), 2,3-heptadienamine (4) and 4,5,5-trimethyl-2,3-heptadienamine (6). Silver tetrafluoroborate (10–20 mg; 0.05–0.1 mmol) was added to a solution of the amine (1–2 mmol) in chloroform (1 ml). The mixture was stirred for 5 h at room temperature. Saturated NaCl-solution (0.1 ml) was added to precipitate the silver (shaking of the mixture) and the mixture was diluted with 10 ml of ether. The mixture was dried over K₂CO₃–Na₂SO₄ and filtered. The pyrrolines were precipitated as oxalates from the filtrate.

1-Benzyl-3-pyrroline (2). ¹H NMR: δ 7.4–7.1 (m, 5 H), 5.72 (s, 2 H), 3.76 (s, 2 H), 3.45 (s, 4 H). The oxalate, obtained in 90 % yield from the allene **1**, was recrystallized from acetone, m.p. 133–134 °C. Anal. C₁₃H₁₅NO₄: C, H, N.

2-Propyl-3-pyrroline (5). ¹H NMR: δ 5.78 (s, 2 H), 4.0–3.6 (two broad m, 3 H), 2.2 (broad s, 1 H), 1.5–1.3 (m, 4 H), 0.93 (t, 3 H). The oxalate, obtained in 85 % yield from the allene **4**, was recrystallized from acetone–EtOH, m.p. 103–104 °C. Anal. C₉H₁₅NO₄: C, H, N.

2-tert-Butyl-2-methyl-3-pyrroline (7). ¹H NMR: δ 5.72 (s, 2 H), 3.70 (AB-quartet, 2 H), 1.9 (broad s, 1 H), 1.16 (s, 3 H), 0.92 (s, 9 H). The oxalate, obtained in 90 % yield from the allene **6**, was recrystallized from acetone–EtOH, m.p. 183–185 °C. Anal. C₁₁H₁₉NO₄: C, H, N.

2,4-Dimethyl-3-pyrroline (9) was isolated from preparative GLC runs of the allenic amine **8**

* Part XVII, see Ref. 1.

(20 % SE-30 on Chromosorb W, 170 °C). ¹H NMR: δ 5.4–5.2 (m, 1 H), 4.2–3.8 (m, 1 H), 3.7–3.5 (m, 2 H), 1.9–1.7 (m, 1+3 H), 1.15 (d, 3 H).

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