Stereoselective Synthesis of 2,4-Diamino-2-alkenes (γ-Aminoenamines Formally Derived from 1-Alkenyl Methyl Ketones) *via* Catalytic Aminomercuriation of 3-Alken-1-ynes

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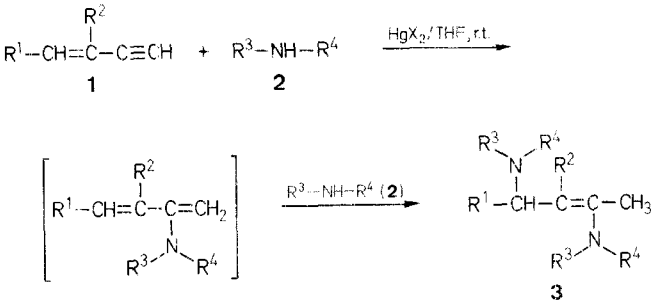
Several hitherto unknown 2,4-diamino-2-alkenes were prepared by the reaction of 3-alken-1-ynes with secondary amines in the presence of catalytic amounts of mercury(II) salts in a one-pot procedure.

We have recently reported that 3-alken-1-ynes behave as 1-alkenyl methyl ketone synthons in catalytic aminomercuriation reactions leading to 1-aza- and 2-morpholino-1,3-dienes[1]. In these processes, the reaction conditions and the nature of the starting enyne proved to be critical, since variations of one or both of these factors substantially alter the reaction products. 1,3-Diamino-1-alkenes (γ-aminoenamines derived from 2-alkenals) have been prepared from 2-alkenals and aminosilanes[2]; the direct synthesis of this little known class of compounds from 2-alkenals and secondary amines[3,4] is difficult. We have now tested the aminomercuriation of 3-alken-1-ynes (**1**) as an approach to the analogous 2,4-diamino-2-alkenes (**3**) which can be regarded as γ-aminoenamines formally derived from 1-alkenyl methyl ketones or enamines derived from 2-aminoalkyl methyl ketones and which have to our knowledge hitherto not been described.



Enediamines **3a–e**, derived from aliphatic amines, are obtained using mercury(II) acetate as catalyst. They are sensitive compounds which must be handled under rigorously anhydrous conditions and which decompose on

Table 1. 2,4-Diamino-2-alkenes (γ-Aminoenamines, **3**) Prepared

3	R^1	R^2	R^3	R^4	Yield [%][a]	Condensation Temperature [°C][b]	Molecular Formula[c]
a	CH_3	H		$-(CH_2)_5-$	43	85–95	$C_{15}H_{28}N_2$ (236.4)
b	CH_3	H		$-(CH_2)_2-O-(CH_2)_2-$	55	85–95	$C_{13}H_{24}N_2O_2$ (240.3)
c	C_2H_5	H		$-(CH_2)_5-$	52	90–100	$C_{16}H_{30}N_2$ (250.4)
d	C_2H_5	H		$-(CH_2)_2-O-(CH_2)_2-$	70	90–100	$C_{14}H_{26}N_2O_2$ (254.4)
e	n-C_3H_7	H		$-(CH_2)_2-O-(CH_2)_2-$	56	100–110	$C_{15}H_{28}N_2O_2$ (268.4)
f	H	CH_3	C_6H_5	CH_3	61	180–200	$C_{19}H_{24}N_2$[d] (280.4)
g	H	CH_3	C_6H_5	C_2H_5	54	–[e]	$C_{21}H_{28}N_2$ (308.5)

[a] Yield of crude reaction product, based on **1**.
[b] Oil bath temperature for trap-to-trap condensation at 0.001 torr.
[c] Satisfactory microanalyses obtained: C ±0.33, H ±0.25, N ±0.35.
[d] MS: $m/e = 280$ (M^+).
[e] Decomposed on attempted distillation or trap-to-trap condensation.

Table 2. NMR-Spectral Data for Compounds **3**

3	^{1}H-NMR ($CDCl_3$)[a] δ [ppm]	^{13}C-NMR (neat/TMS_{int})[a] δ [ppm]
a	1.0 (d, 3H); 1.2–1.55 (m, 12H); 1.65 (s, 3H); 2.1–2.5 (m, 4H); 2.55–2.8 (m, 4H); 2.8–3.1 (m, 1H); 4.3 (d, 1H)	16.7 (q); 20.0 (q); 25.7 (t); 26.0 (t); 27.0 (t); 27.5 (t); 50.5 (t); 51.3 (t); 58.9 (d); 107.7 (d); 146.0 (s)
b	1.15 (d, 3H); 1.8 (s, 3H); 2.35–2.65 (m, 4H); 2.7–2.9 (m, 4H); 2.9–3.3 (m, 1H); 3.5–3.85 (m, 8H); 4.35 (d, 1H)	16.1 (q); 20.2 (q); 50.0 (t); 51.3 (t); 58.8 (d); 67.5 (t); 68.0 (t); 107.1 (d); 145.8 (s)
c	0.9 (t, 3H); 1.1–1.65 (m, 14H); 1.75 (s, 3H); 2.2–2.6 (m, 4H); 2.65–3.1 (m, 5H); 4.3 (d, 1H)	11.7 (q); 16.9 (q); 24.4 (t); 25.8 (t); 26.1 (t); 27.1 (t); 27.6 (t); 50.7 (t); 51.2 (t); 65.3 (d); 105.0 (d); 147.3 (s)
d	0.85 (t, 3H); 1.2–1.6 (m, 2H); 1.8 (s, 3H); 2.2–2.5 (m, 4H); 2.7–3.0 (m, 5H); 3.45–3.75 (m, 8H); 4.2 (d, 1H)[b]	11.3 (q); 16.1 (q); 26.6 (t); 49.9 (t); 50.8 (t); 64.7 (d); 67.4 (t); 67.8 (t); 104.1 (d); 146.9 (s)
e	0.9 (t, 3H); 1.1–1.5 (m, 5H); 1.75 (s, 3H); 2.25–2.55 (m, 4H); 2.65–3.1 (m, 5H); 3.4–3.75 (m, 8H); 4.2 (d, 1H)[b]	14.9 (q); 16.0 (q); 20.5 (t); 36.3 (t); 49.4 (t); 49.9 (t); 62.9 (d); 67.3 (t); 67.8 (t); 104.1 (d); 146.8 (s)
f	1.65 (s, 3H); 1.75 (s, 3H); 2.8 (s, 3H); 2.95 (s, 3H); 3.9 (s, 2H); 6.5–6.8 (m, $6H_{arom}$); 7.05–7.4 (m, $4H_{arom}$)	14.7 (q); 15.7 (q); 37.0 (q); 38.7 (q); 55.1 (t); 113.1 (d); 113.6 (d); 117.2 (d); 117.5 (d); 130.0 (2d); 131.8 (s); 137.3 (s); 148.1 (s); 150.9 (s)[c]
g	0.9–1.4 (m, 6H); 1.7 (s, 3H); 1.85 (s, 3H); 3.1–3.6 (m, 4H); 3.95 (s, 2H); 6.5–6.9 (m, $6H_{arom}$); 7.1–7.45 (m, $4H_{arom}$)	12.2 (q); 13.9 (q); 15.3 (q); 16.9 (q); 38.9 (t); 45.1 (t); 52.0 (t); 113.3 (d); 113.8 (d); 116.6 (d); 117.5 (d); 129.8 (2d); 132.0 (s); 135.3 (s); 147.4 (s); 149.5 (s)[c]

[a] Recorded on a Varian FT-80A spectrometer.
[b] In CCl_4.
[c] In $CDCl_3$.

standing. Their acid hydrolysis affords the corresponding β-aminoketones in almost quantitative yield. On the other hand, enediamines **3f, g** which are derived from aromatic amines are best obtained using mercury(II) chloride. They are so stable that they are not affected by sodium borohydride reduction in alkaline medium which is part of the work-up and improves the yield. Spectrometric data of all enediamines **3** reveal the presence of a single stereoisomer, probably the *E*-form which is obtained due to steric reasons.

The 3-alken-1-ynes **1** are prepared as described[5], dried with anhydrous sodium sulfate and molecular sieves in tetrahydrofuran at 40–50 °C, and stored under argon over molecular sieves.

2,4-Diamino-2-alkenes 3; General Procedures:

2,4-Diamino-2-alkenes **3a–e**: Dry mercury(II) acetate (4.78 g, 15 mmol) is added under argon during ~ 10 min to a stirred solution of a dry 3-alken-1-yne (**1**; 20 mmol) and a dry secondary aliphatic amine (**2**; 60 mmol) in dry tetrahydrofuran (60 ml). The mixture is stirred for 12 h at room temperature, then filtered under argon, and the liquid phase is evaporated at 0.05 torr. The residue is digested with dry hexane (3 × 20 ml), the solution filtered under argon, and the filtrate concentrated at 0.05 torr. The crude product is a nearly pure, yellow oil which can be trap-to-trap condensed in vacuo.

2,4-Diamino-2-alkenes **3f, g**: Mercury(II) chloride (1.36 g, 5 mmol) is added to a stirred solution of 2-methyl-1-buten-3-yne (**1**, $R^1 = H$, $R^2 = CH_3$; 1.0 ml, 10 mmol) and a secondary aromatic amine (**2**; 40 mmol) in tetrahydrofuran (40 ml). The mixture is stirred at room temperature for 48 h, the mercury(II) species are reduced with sodium borohydride (0.19 g, 5 mmol) in aqueous 3 molar sodium hydroxide (15 ml), the precipitated metallic mercury is filtered off, and the filtrate is extracted with ether (3 × 20 ml). The organic layer is dried with sodium sulfate and the volatile components are evaporated under reduced pressure (15 and 0.001 torr, successively). The crude product is a nearly pure, brown oil which in the case of **3f** can be trap-to-trap condensed in vacuo.

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