One-Pot Synthesis of Hexatriynediamines[1]

Dieter Faul, Edith Leber, Gerhard Himbert*

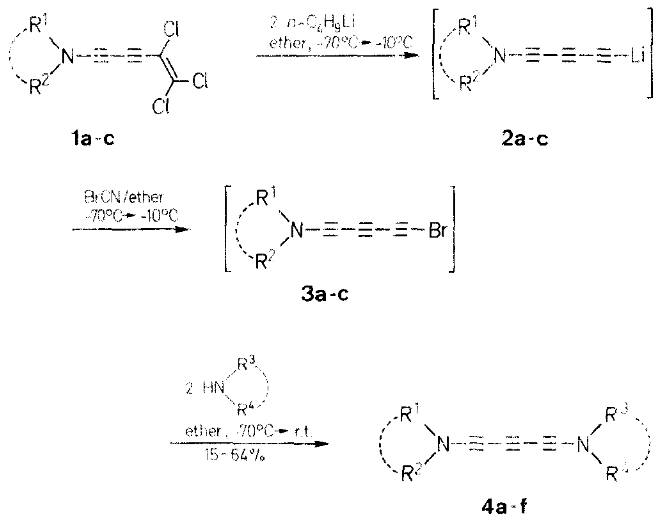
Fachbereich Chemie der Universität Kaiserslautern, Postfach 3049, D-6750 Kaiserslautern, West Germany

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

By combining the perchlorobutenyne of *Roedig*[2] with the lithium aminoethynides of *Ficini*,[3] the preparation of 5,6,6-trichloro-5-hexene-1,3-diynylamines **1** can be performed in fairly good yields.[1,4] In analogy with our synthesis of butadiyne diamines[5] *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 weaks in a



1–3	R^1	R^2
a	CH_3	C_6H_5
b	$-(CH_2)_2O(CH_2)_2-$	
c	C_2H_5	C_2H_5

4	R^1	R^2	R^3	R^4
a	CH_3	C_6H_5	$-(CH_2)_2O(CH_2)_2-$	
b	CH_3	C_6H_5	$-(CH_2)_5-$	
c	$-(CH_2)_2O(CH_2)_2-$		$-(CH_2)_2O(CH_2)_2-$	
d	$-(CH_2)_2O(CH_2)_2-$		$-(CH_2)_5-$	
e	$-(CH_2)_2O(CH_2)_2-$		$-(CH_2)_4-$	
f	$-(CH_2)_2O(CH_2)_2-$		C_2H_5	C_2H_5
f'	C_2H_5	C_2H_5	$-(CH_2)_2O(CH_2)_2-$	

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 ^{13}C-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 ^{1}H-NMR spectra were recorded on a Perkin-Elmer 394 infrared spectrophotometer and on a Varian EM 390 spectrometer, respectively. The described ^{13}C-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 C,H,N 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 *n*-butyllithium in hexane (70 ml, 1.6 molar, 112 mmol) first the same volume of anhydrous ether (70 ml) and then a solution of **1a–c** (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, 53 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 HNR^{3}R^4 (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. Hexatriynediamines **4** Prepared

Product **4**	Yield (%)	m.p. (°C)[a] (solvent)	Molecular Formula[b]	IR ν (cm^{-1})	^{1}H-NMR ($CDCl_3/TMS_{int}$) δ (ppm)	^{13}C-NMR ($CDCl_3/TMS_{int}$) δ (ppm)
a	47	124–125 (CH_2Cl_2/ether)	$C_{17}H_{16}N_2O$ (264.3)	2190 vs 1592 1580 w 1490 s	3.10 (m, 4H, NCH_2); 3.28 (s, 3H, NME); 3.67 (m, 4H, OCH_2); 6.75–7.45 (m; 5H)	86.11, 79.81, 69.86 67.68, 59.20, 54.01 (6s; acetylenic-C), 39.30 (q); 51.45 (t); 66.08 (t); 114.97, 122.05, 129.47 (3d); 143.91 (s)
b	64	114–115 (ether)	$C_{18}H_{18}N_2$ (262.4)	2190 vs 1596 s 1580 w 1494 s	1.57 (m, 6H, $3CH_2$); 3.15 (m, 4H, NCH_2; 3.31 (s, 3H, NMe); 6.8–7.4 (m; 5H)	–
c	53	134–135 (CH_2Cl_2/ether)	$C_{14}H_{16}N_2O_2$ (244.3)	2190 vs	3.13 (m, 8H, NCH_2); 3.67 (m, 8H, OCH_2)	85.24, 67.93, 53.95 (3s; acetylenic-C); 66.07 (t); 51.46 (t)
d	26	125–126 (ether)	$C_{15}H_{18}N_2O$ (242.3)	2190 vs	1.57 (m, 6H, $3CH_2$); 3.16 (m, 8H, NCH_2); 3.72 (m, 4H, OCH_2)	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)
e	15	124–125 (CH_2Cl_2)	$C_{14}H_{16}N_2O$ (228.3)	2170 vs 2120 s	1.68–1.96 (m, 4H); 3.0–3.4 (m, 8H, NCH_2); 3.6–3.8 (m, 4H, OCH_2)	–
f/f′	22/15	55–56 (ether/petroleum ether)	$C_{14}H_{18}N_2O$ (230.3)	2180 vs	1.18 (t, 6H, $J = 7$ Hz, NCH_2CH_3); 3.00 (q, 4H, $J = 7$ Hz, NCH_2CH_3); 3.12 (m, 4H, NCH_2); 3.70 (m, 4H, OCH_2)	–

[a] Decomposition.

[b] 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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