Synthesis of a Conjugated Triene Diamine [1,2-Bis(β-dimethylaminovinyl)-cyclopentene] through the Isomerization of an αω-Diaminonadiyne

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Summary The diacetylenic diamine (**3a**) rearranges instantaneously and quantitatively, *via* its lithium derivative, to the triene diamine (**4a**).

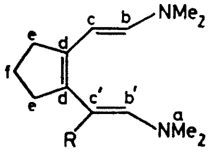
PROP-2-YNYLIC tertiary amines (**1**) are known to give a lithium derivative with Bu^nLi, probably possessing the allenic structure (**2**), and which can be useful synthetically.[1,2] As we were interested in the possibility of using diprop-2-ynylic diamines (**3**) for similar purposes, we have studied their metallation.

$R^2C{\equiv}CCH_2NR^1_2$ (**1**) $R^2CLi{=}C{=}CHNR^1_2$ (**2**)

$R^1_2NCH_2C{\equiv}C[CH_2]_nC{\equiv}CCH_2NR^1_2$

(**3**) **a**; $n = 3$, $R^1 = Me$

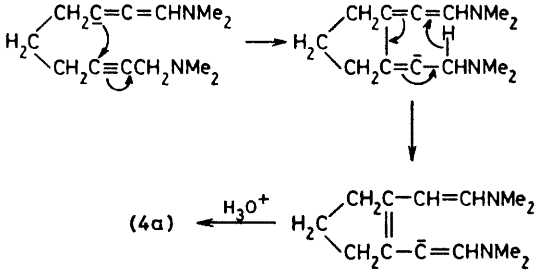
Starting with compound (**3a**),[3] we noticed that when treated with Bu^nLi in tetrahydrofuran (THF) at −10 °C, it yielded a monolithio-derivative which, on protonation, gave quantitatively 1,2-bis(β-dimethylaminovinyl)cyclopentene (**4a**), which is a solid, m.p. 68 °C, subliming at 100 °C and 0.1 mmHg, and darkening rapidly in the air, giving rise to a polymer insoluble in the usual solvents. It can nevertheless be stored for several months in THF at −30 °C.



(**4**)

a, R = H
b, R = D

The structure of (**4a**) follows from its i.r. [ν_{max} (KBr pellet): 1625 (strong), and 1330—1350, 1090, and 920 (weaker) cm^{-1}], ^{1}H n.m.r. [δ (CCl_4; Me_4Si): a, 2·70 (s); b, 5·95 (d); c, 520 (d); e, 2·35 (t); and f, 1·80 (m); J_{bc} 14 Hz], and ^{13}C n.m.r. spectra [δ (CD_3SOCD_3–CH_3SOCH_3): a, 40·35; b, 138·75; c, 95·85; d, 127·95; e, 33·20; and f, 21·20 p.p.m.], and the ^{1}H n.m.r. spectrum of the deuteriated product (**4b**), obtained when the reaction mixture is worked-up with D_2O (peak of the c proton reduced by one half, broadened peak of the b′ proton inserted inside the b doublet).



SCHEME.

In the presence of Raney nickel, (**4a**) absorbs **3** mol. equiv. of hydrogen, leading to the known 1,2-bis(β-dimethylaminoethyl)cyclopentane.[4]

This reaction does not take place with other compounds (**3**) in which *n* = 2 or **4**, nor with compounds bearing other nitrogen substituents (diethylamino or morpholino). When the amino-group in (**3**) is replaced by MeO, the starting material is also recovered unchanged.

We have no conclusive evidence concerning the mechanism of this rearrangement. However, it seems reasonable to assume the reactions in the Scheme.

The literature gives some examples of spontaneous cyclizations of δ-acetylenic carbanions,[5] and so the rearrangement of the diamine (**3a**) is not totally unexpected. However, the extreme ease with which the reaction takes place and the fact that it gives rise to an apparently new type of compound makes it worthy of note.

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