SYNTHESIS OF CONJUGATED TRIENE-DIAMINES
## THROUGH THE ISOMERIZATION OF αω-DIAMINONONADIYNES

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Abstract: Diacetylenic diamines $\underline{1}$ rearrange via their lithio derivatives to the conjugated triene-diamines $\underline{2}$. The cyclization proceeds more or less easily according to the nature of N-substituents. It can also be extended to the hydroxy derivatives of $\underline{1}$.

We have reported recently[1] the instantaneous and quantitative cyclization of the bis-acetylenic Mannich base $\underline{1a}$, via its monolithium derivative, to the conjugated triene-diamine $\underline{2a}$:
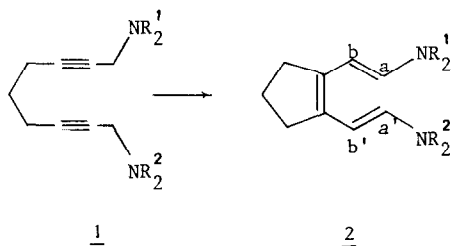

a) $R^1 = R^2 = Me$

b) $R^1 = R^2 = Et$

c) $R^1_2 = R^2_2 = -(CH_2)_2O(CH_2)_2-$

d) $R^1_2 = R^2_2 = -(CH_2)_4-$

e) $R^1 = Me$, $R^2_2 = -(CH_2)_2O(CH_2)_2-$

$\underline{1}$ and $\underline{2}$ are not affected under the same conditions.

This new reaction has now been more thoroughly investigated. We intended, first of all, to check the validity of the mechanism[1] proposed for this rearrangement, then to try to generalize this reaction to other $\underline{1}$'s as well as to related compounds possessing a fonctionalized trimethylene chain such as $\underline{3}$ and $\underline{4}$, and finally to study the chemical behaviour of $\underline{2a}$ and eventually of its analogues.

The cyclization reaction, performed with dideuterated $\underline{1a}$[2] afforded almost exclusively the triene-diamine $\underline{2a}$-d_2 arising, as expected, from the anion formed by abstraction of a proton rather than of a deuteron.[3]

3   **4**
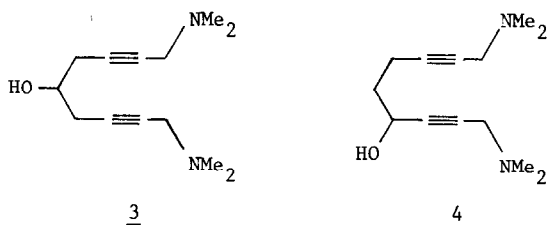
This result confirms the postulated mechanism which involves (cf. scheme) the cyclization of the initially formed allenic carbanion followed by a 1,5-sigmatropic hydrogen (deuterium) shift from one side chain to the other.
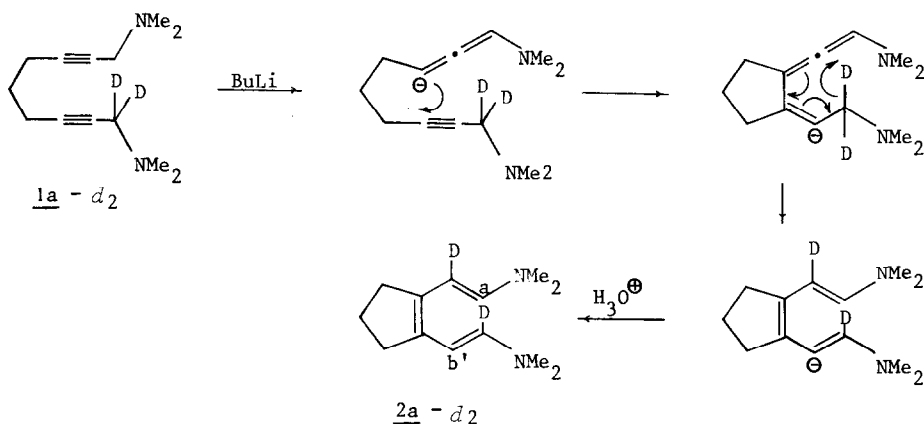

Scheme

Contrary to <u>1b</u> and <u>1c</u> which, as said above, give no detectable amounts of cyclized material in 15mn at -10°, their analogues <u>1d</u> and <u>1e</u> prepared by two successive Mannich reactions on 1,6-heptadiyne, show by n.m.r. spectrometry the appearance of small quantities of the corresponding <u>2</u>'s. An increase of the contact time to 80 hrs brings it to completion. <u>1b</u> can also be entirely transformed into <u>2b</u>, but 2 weeks are then required. A rise of the temperature leads to larger proportions of polymers.

This reaction was also extended to the compounds <u>3</u> and <u>4</u> which were prepared as follows:

A Mannich reaction performed on $HO(CH_2C\equiv CH)_2$[4] afforded **3** in 80% yield.

$Me_3SiC\equiv C(CH_2)_3OH$[5] , oxidized by pyridinium chlorochromate[6] , gave $Me_3SiC\equiv C(CH_2)_2CHO$ (45%) which, with lithiated $Me_2NCH_2C\equiv CH$ afforded, after desilylation, $Me_2NCH_2C\equiv CCH(OH)(CH_2)_2C\equiv CH$. The latter led to **4** by a Mannich condensation.

Treated with 2 equivalents of BuLi, **3** disappears after 2 weeks. The triene-diamine **5** is then formed accompanied by an important amount of tars.


5	**6**
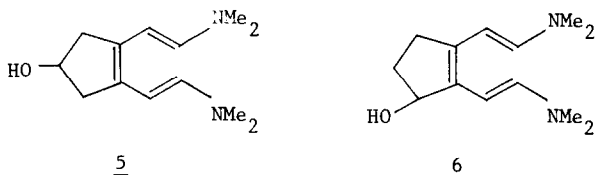
With the same reagent, **4** reacts more rapidly; after 1 hr, more than one half of the diamine has disappeared. The n.m.r. spectrum of the reaction mixture shows the presence of vinylic protons together with by-products.

Due to the lack of stability of the triene-diamines **2** as experienced on **2a**, we did not try to purify them. They could however be characterized by their n.m.r. data recorded immediately after their preparation.

	a	a'	b	b'
			δ	
2b		5,86		5,17
2d		6,13		5,08
2e	5,98	6,14	5,28	5,58
5		5,92		5,13
6	6,01	6,42	5,08	4,76

The solvent is CCl_4 except for **2e** which was dissolved in $CDCl_3$

The chemical behaviour of these substances is being investigated. In the presence of acid they yield immediately a black polymer. Therefore we were unable either to prepare their salts or to hydrolyze them to the corresponding dialdehyde. We succeeded nevertheless in transforming **2a** into the dioxime **7** in 70% yield by refluxing with an hydro-alcoholic solution of hydroxyl-ammonium acetate. **7** melts around 140°. It is a mixture of ZZ, EE and ZE isomers with a large predominance of the E n.m.r. signal[7] .

7   8
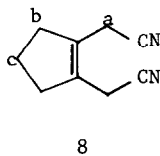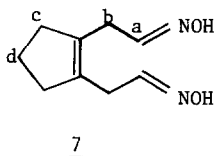
Refluxing 7 for a short time with acetic anhydride affords the dinitrile [8] 8 in 60% yield ,m.p. 65° .

NOTES AND REFERENCES

1. R.Epsztein and B.Herman, *J.Chem.Soc. Chem. Comm.*, 1980, 1250

2. 1a-d_2 was prepared from the mono-Mannich base of 1-6-heptadiyne by a second Mannich condensation using deuterated paraformaldehyde. Its n.m.r. spectrum differs from 1a only in that the area of his NCH_2 signal (CCl_4,TMS,3.13ppm,t) corresponds to two protons instead of four.

3. The kinetic isotope effect is expected to have at ~-10°C approximately the value of 9 (cf. E.Buncel, Carbanions: Mechanistic and isotopic aspects; Elsevier 1975, p.23). The n.m.r. spectrum of the reaction product shows two broadened peaks of one proton each at 5.93 and 5.18 ppm representing resp. a and b' hydrogen atoms of 2a-d_2 (in 2a the a and b signals are doublets and correspond to two protons each). Both have a spred out foot (cf.figure) doubtlessly due to the doublets of monodeuterated 2a arising from the carbanion formed by initial deuteron abstraction and which should represent about 1/10 of the total.

2a - d_1

5,93   5,18
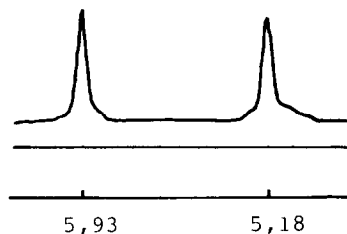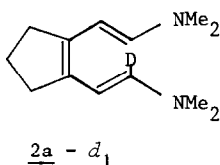
4. M.Gaudemar, *Ann. Chim.*,1956, 1, 161

5. J.S.Cochrane and J.R.Hanson, *J. Chem. Soc. Perk.I*, 1972, 361

6. E.J.Corey and J.W.Suggs, *Tetrahedron Letters*, 1975, 2647

7. n.m.r.(DMSO) a: 6.59,t-7.22,t; b:3.05,d-2.92,d(resp. E and Z signals; cf. G.J.Karabatsos and R.A.Taller, *Tetrahedron*, 1968, 24, 3347); c: 2.32,m; d: 1.76,m.

   I.R. (KBr pellet) wide band around 3200 cm^{-1}(OH); narrower band at 1655 cm^{-1} (C=N).

8. n.m.r. (CDCl$_3$) a: 3.19,s; b: 2.55,m; c: 1.95,m.

   I.R. (CHCl$_3$) 2250 cm^{-1} (C≡N)