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THE PREPARATION OF CONJUGATED TRIENEDIAMINES FROM 1,9-DIAMINONONA-2,7-DIYNES AND THEIR USE IN SYNTHESIS

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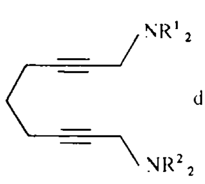
Abstract The preparation of conjugated trienediamines from 1,9-bis-dialkylaminonona-2,7-diynes **1** is described. Some reactions of these compounds are reported, more particularly the addition of hydrogen cyanide affording a mixture of diastereoisomeric bis-α-aminonitriles **12** which, in turn, can be used for synthetic purposes.

In two previous short communications[1,2] we reported the synthesis of the conjugated trienediamines **2** from the diacetylenic diamines **1a**–**1d** upon treatment with *n*-butyllithium in tetrahydrofuran. A mechanism was proposed in order to explain this transformation (Scheme 1).[2] It was supported by the fact that the carbanion generated from **1a** affords, with D_2O, monodeuterated **2a**–d_1 whereas, when the rearrangement is performed with dideuterated **1a**–d_2, **2a**–d_2 is formed predominantly. The localization of the D atoms was effected by means of ^{1}H-NMR.[2] The reaction could be extended to the hydroxylated analogues **4** and **5** of **1a** which yielded, respectively, **6** and **7**.[2] The NMR data of these trienediamines are shown in Table 1.



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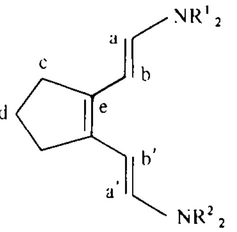

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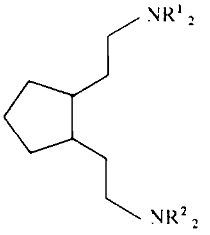
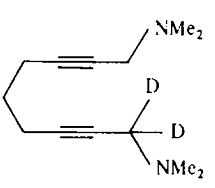
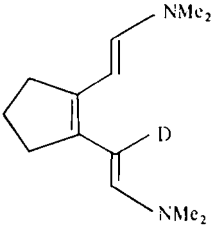


3

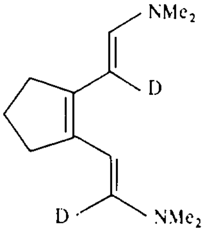
a $R^1 = R^2 = Me$
b $R^1 = R^2 = Et$
c $R^1{}_2 = R^2{}_2 = (CH_2)_4$
d $R^1{}_2 = Me$, $R^2{}_2 = \begin{matrix}-(CH_2)_2 \\ -(CH_2)_2\end{matrix}\!\!>O$
e $R^1{}_2 = R^2{}_2 = \begin{matrix}-(CH_2)_2 \\ -(CH_2)_2\end{matrix}\!\!>O$



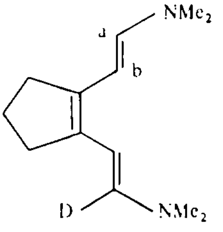
1a–d_2



2a–d_1

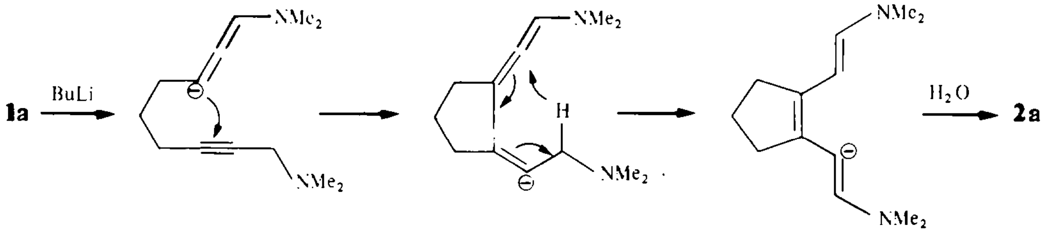


2a–d_2

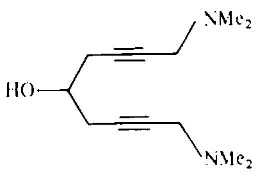


2a–d'

An investigation of the synthetic possibilities offered by this new series of compounds was undertaken but, owing to their lack of stability, especially under acidic conditions, it did not seem very promising and only two reactions could be performed. Catalytic hydrogenation afforded the saturated diamines **3** and treatment of **2a** with hydroxylamine, in the presence of acetic acid, yielded the dioxime **8** of the corresponding dialdehyde



Scheme 1.



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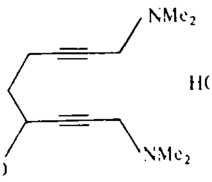

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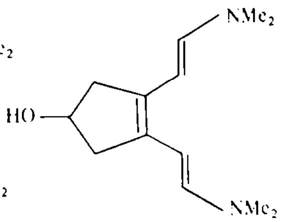

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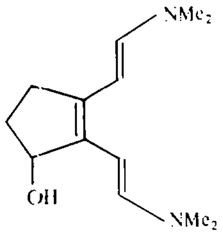

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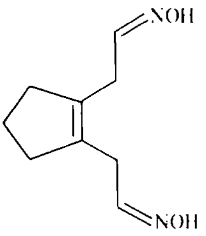
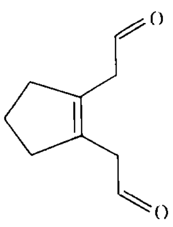
9. Compound **8** could be dehydrated with acetic anhydride giving rise to the dinitrile **10**.



8



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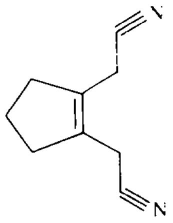
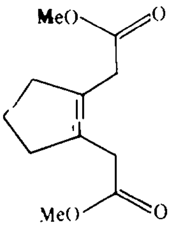


10



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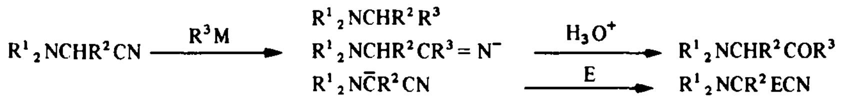
This work has now been elaborated further. In the present paper we report some new developments concerning our investigations in this area and describe the experimental details related to the previous study.[1,2] In the first place it seemed important to us to return to the argument which allowed us to elucidate the mechanism of the rearrangement. The very large isotopic effect observed when the transformation was carried out with **1a**-d_2 was of considerable help. The trienediamine **2a** d_2 is, indeed, so predominant that there is no ambiguity in interpreting the ^{1}H-NMR spectrum of the reaction product. Thus, instead of the two doublets corresponding to the two pairs of vinylic protons of **2a** which resonate at δ 5.20 and 5.95, two broadened peaks of intensity corresponding to one proton each are now present at the same frequencies. Both have a broadened foot which may be due to the minor **2a**-d' component arising from an initial D abstraction and in which the coupling still exists between protons a and b. Of course, such an isotopic effect might seem surprisingly large, however, it can be calculated as close to 9 at *ca* $-10°$, which is the reaction temperature.[3] The above result could be confirmed by mass spectroscopy which shows, in the reaction mixture, two molecular ion peaks, *m/z* 208 for **2a** d_2 and *m/z* 207 for **2a**-d' in a ratio of *ca* 10:1.

Among the new results let us mention first the methanolysis under acidic conditions of the dinitrile **10** which led to the diester **11**. But what we were interested in, above all, was the possibility of taking advantage of the presence of the two enamine groupings for synthetic purposes. Enamines are known to react, mainly as iminium derivatives with various nucleophiles.[4] Unfortunately, this kind of reaction could not be performed in our case since attempts to prepare iminium salts from **2** failed. There was, however, another possibility offered by the ability of enamines to add hydrogen cyanide in a weakly acidic medium giving rise to α-aminonitriles[4] which, in turn, can be brought to react with nucleophiles.[4,5] This property could be applied to the trienediamine **2a** which added 2 mols of hydrogen cyanide affording, in 80% yield, the bis-aminonitrile **12** as a mixture of diastereoisomers which could be separated by crystallization. The configuration of the diastereoisomers has not yet been established, however.

Table 1

Compound	a	a′	b	b′		
2a	5.95 (*d*) 2H		5.20 (*d*) 2H		2.70 (*s*) 6H (NMe$_2$)	$J_{a,b} = 14$ Hz
2a-d_1	5.95 (*d*) 1H	5.95 (*s*) 1H	5.20 (*d*) 1H			$J_{a,b} = 14$ Hz
2a d_2	5.93 (*s*) 1H			5.18 (*s*) 1H	—	
2b	5.86 (*d*) 2H		5.17 (*d*) 2H			$J_{a,b} = 13$ Hz
2c	6.13 (*d*) 2H		5.08 (*d*) 2H			$J_{a,b} = 13$ Hz
2d	5.98 (*d*) 1H	6.14 (*d*) 1H	5.28 (*d*) 1H	5.58 (*d*) 1H		$J_{a,b} = J_{a',b'} = 14$ Hz
6	5.92 (*d*) 2H		5.28 (*d*) 2H		—	$J_{a,b} = 14$ Hz
7	6.01 (*d*) 1H	6.42 (*d*) 1H	5.08 (*d*) 1H	4.76 (*d*) 1H	—	$J_{a,b} = J_{a',b'} = 13$ Hz



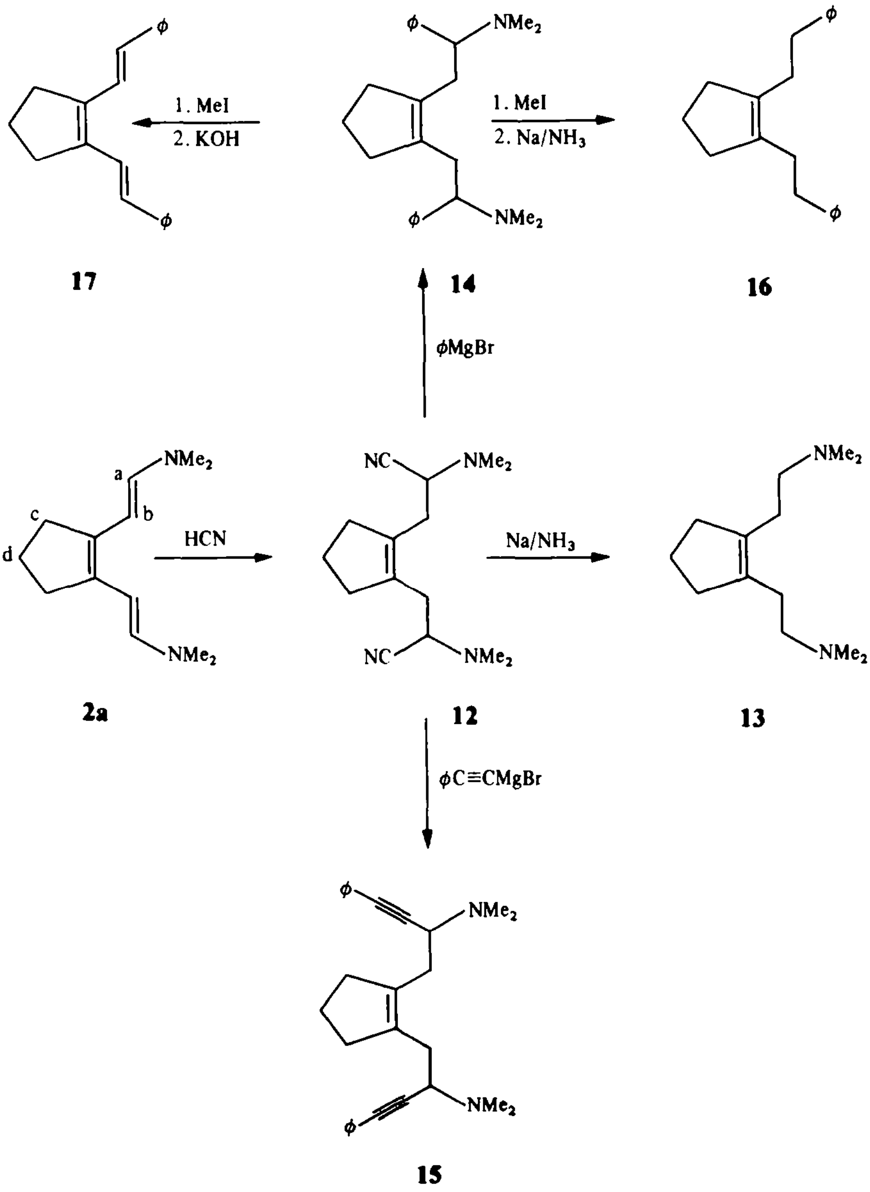
$$R^1_2NCHR^2CN \xrightarrow{R^3M} \begin{array}{l} R^1_2NCHR^2R^3 \\ R^1_2NCHR^2CR^3=N^- \xrightarrow{H_3O^+} R^1_2NCHR^2COR^3 \\ R^1_2N\bar{C}R^2CN \xrightarrow{E} R^1_2NCR^2ECN \end{array}$$

Scheme 2.

Reduction of **12** with sodium in liquid ammonia[6,7] yielded the ethylenic diamine **13**. α-Aminonitriles can react in three ways with organometallics (Scheme 2). They may undergo either substitution of the cyano group,[4,5,8] addition on the cyano triple bond,[8] or proton abstraction.[9–13]

We shall report here the results which we obtained by treating the bis-aminonitrile **12** with Grignards which mainly give rise to the first kind of transformation (Scheme 3).

Both diastereoisomers were reacted with phenylmagnesium bromide yielding the same mixture of diastereoisomeric diamines **14** which is in agreement with an S_N1 mechanism.[8] In the same way, phenylethynylmagnesium bromide led to the diacetylenic diamine **15**, also as a mixture of diastereoisomers. Compound **14** underwent reductive deamination via its methiodide on treatment with sodium in liquid ammonia leading to 1,2-bis-β-phenylethylcyclopentene (**16**). Heated with potassium



Scheme 3.

Table 2

Compound	a	b	c	d	NMe_2	
8[*]	6.59 (*t*) 7.22 (*t*)	3.05 (*d*) 2.92 (*d*)	2.32 (*m*)	1.76 (*m*)	—	
10	—	3.19 (*s*)	2.55 (*m*)	1.95 (*m*)	—	
11	—	3.10 (*s*)	2.42 (*t*)	1.84 (*m*)		MeO: 3.63 (*s*)
12[†] M.p. 94°	3.63 (*dd*)	(1) 2.66 (*dd*) (2) 2.64 (*dd*)	2.43 (*t*)	1.86 (*m*)	2.33 (*s*)	J_{b_1,b_2} = 14 Hz J_{a,b_1} = 10 Hz J_{a,b_2} = 5.5 Hz
12[†] M.p. 95°	3.62 (*dd*)	(1) 2.60 (*dd*) (2) 2.50 (*dd*)	2.42 (*t*)	1.86 (*m*)	2.32 (*s*)	J_{b_1,b_2} = 14 Hz J_{a,b_1} = 8.5 Hz J_{a,b_2} = 7 Hz
13	2.22–2.42			1.78 (*m*)	2.24	—
14[‡]	3.08 (*m*)	2.15–2.65			2.14 2.16	Ph: 7.18
15[‡]	3.70 (*m*)	2.30–2.80		1.87 (*m*)	2.30 2.33	Ph: 7.34
16	2.10–2.67			1.78	—	Ph: 7.05–7.30
17[†]	7.41 (*d*)	6.51 (*d*)	2.72 (*t*)	1.93 (*m*)		Ph: 7.17–7.52 ($J_{a,b}$ = 17 Hz)

[*] Mixture of *E*- and *Z*-isomers.[17]

[†] Recorded at 400 MHz.

[‡] Mixture of *meso*- and DL-diastereoisomers.

hydroxide in dilute methanol the same methiodide afforded 1,2-bis-β-styrylcyclopentene (**17**). The NMR data of these new compounds are presented in Table 2.

Other reactions of the trienediamines **2** are being investigated, but it may be already concluded from the above results that these compounds are interesting intermediates for various syntheses. Moreover, the possibility of preparing, from compounds **4** and **5**, trienediamines carrying functional groups on the five-membered ring, suggests that this may open a new and convenient approach to elaborate molecules such as prostaglandins.

EXPERIMENTAL

Most of the ^{1}H-NMR data were recorded on a Perkin-Elmer R32 spectrometer at 90 MHz in $CDCl_3$. TMS was used as internal reference. For some compounds, a 400 MHz spectrometer designed at the Institut d'Electronique Fondamentale of the University of Paris Sud was used. The ^{13}C-NMR spectra were recorded, using Fourier Transform, on a Bruker WP60 spectrometer at 90 MHz. The mass spectra were recorded on an A.E.I. Kratos MS50 spectrometer.

1,9-Bis-dimethyl- and diethylamino-2,7-diyne, **1a** *and* **1b**, *respectively*. Prepared as described in the lit.[14] from hepta-1,6-diyne, paraformaldehyde and dimethyl(diethyl)amine.

1,9-Dipyrrolidinonona-2,7-diyne (**1c**). B.p. 127°/0.05 mm (found: C, 78.89; H, 10.10; N, 10.78; $C_{17}H_{26}N_2$ requires: C, 79.02; H, 10.14; N, 10.84%) and 1,9-dimorpholinonona-2,7-diyne (**1e**), b.p. 130° (bath temp)/10^{-4} mm. M.p. (Et_2O–hexane) 42° (found: C, 70.47; H, 9.00; N, 9.53; O, 10.94; $C_{17}H_{26}N_2O_2$ requires: C, 70.31; H, 9.02; N, 9.65; O, 11.02%) were obtained in the same way in 80% yield with pyrrolidine and morpholine, respectively.

1-Dimethylamino-9-morpholinonona-2,7-diyne (**1d**). B.p. 115°/0.01 mm (found: C, 72.69; H, 9.65; N, 11.31; O, 6.62; $C_{15}H_{24}N_2O$ requires: C, 72.54; H, 9.74; N, 11.28; O, 6.44%) was prepared by the same method from 1-dimethylamino-octa-2,7-diyne, b.p. 92°/12 mm, which was obtained in 48% yield by treating hepta-1-6-diyne with equimolecular amounts of paraformaldehyde and dimethylamine.

1,9-Bis-dimethylaminonona-2,7-diyn-5-ol (**4**). (Found: C, 70.09; H, 10.09; N, 12.59; O, 7.25; $C_{13}H_{22}N_2O$ requires: C, 70.23; H, 9.93; N, 12.60; O, 7.20%.) Obtained from hepta-1,6-diyn-4-ol, under the same conditions as for the parent hydrocarbon, b.p. 110°/0.01 mm.

1,9-Bis-dimethylaminonona-2,7-diyn-4-ol (**5**). A stirred soln (1 g, 12 mmol) of 1-dimethylaminoprop-2-yne in 10 ml of THF was cooled to −50° under a slow stream of N_2. A 1.5 molar soln (8 ml) of *n*-BuLi in hexane was then added dropwise. After 15 min, a soln of 1.5 g (10 mmol) of 1-trimethylsilylpent-1-yn-5-al[15] in 5 ml of THF was added. After 2.5 hr, a soln of 1 ml of HOAc in 10 ml of Et_2O was dropped into the mixture, followed by 5 ml of H_2O. The organic layer was separated, washed with H_2O and with sat $NaHCO_3$ aq. The soln was dried on K_2CO_3, the solvent was removed *in vacuo* and the residue was distilled in a Büchi 'Kugelrohr' at 120° under 0.1 mm, 1-dimethylamino-8-trimethylsilylocta-2,7-diyn-4-ol (1.6 g) was thus obtained.

The silylated aminoalcohol was refluxed in 10 ml of MeOH with 1.5 g of K_2CO_3 over 1 hr. The solvent was then removed and Et_2O was added. After filtration and evaporation, 0.9 g of crude 1-dimethylamino-octa-2,7-diyn-4-ol was obtained and allowed to react overnight with 2 ml of pyridine and 1 ml of Ac_2O. Pentane (10 ml) and crushed ice were added, followed by solid $NaHCO_3$ until no more CO_2 was evolved. The mixture was then extracted several times with pentane. After drying on K_2CO_3 and evaporation of the solvent, 0.9 g of crude acetate of the above alcohol was obtained. A Mannich reaction was then performed with the aminoester yielding 0.8 g of the crude acetate of **5** which was refluxed in MeOH with 0.8 g of K_2CO_3 for 1 hr. The solvent was then removed and a few drops of H_2O were added. The resulting paste was extracted with Et_2O; the combined Et_2O extracts were dried with K_2CO_3. Evaporation of the solvent and 'Kugelrohr' distillation at 120°/0.005 mm afforded 0.6 g of pure **5**. (Found: C, 70.12; H, 9.95; N, 12.57; O, 6.96; $C_{13}H_{22}N_2O$ requires: C, 70.23; H, 9.93; N, 12.60; O, 7.20%.)

1,1-Dideutero-1,9-bis-dimethylaminonona-2,7-diyne (**1a**–*d_2*). Obtained from 1-dimethylaminoocta-2,7-diyne which was treated in the usual Mannich reaction conditions with dideuterated paraformaldehyde and dimethylamine.

1,2-Bis-β-dimethylaminoethenylcyclopentene (**2a**). A magnetically stirred soln of 7.2 g (35 mmol) of **1a** in 50 ml of THF was cooled to −15° under N_2. A 1.5 molar soln (30 ml) of *n*-BuLi in hexane was then added dropwise and the mixture was kept at the same temp for 0.5 hr. H_2O (5 ml) was then added. After extraction with Et_2O, drying on K_2CO_3 and evaporation of the solvent, 7.25 g of a solid which darkened rapidly on exposure to air was obtained. Sublimation at 120°/0.05 mm afforded 7 g of a light brown solid with m.p. around 60°. It absorbed O_2 rapidly, turning into a dark brown oil. In an inert atmosphere, however, it was fairly stable. IR ν_{max}^{KBr} cm^{-1}: 1625 (strong), 1330–1350, 1090 and 920 (weaker). ^1H-NMR: see Table 1. ^{13}C-NMR (CD_3SOCD_3–MeSOMe): NMe, δ 40.35; a, 138.75; b, 95.85; c, 33.20; d, 21.20; e, 127.95. Due to its instability, no satisfactory elemental analysis could be obtained. (Found: C, 74.61; H, 10.62; N, 12.91; $C_{13}H_{22}N_2$ requires: C, 75.67; H, 10.75; N, 13.58%.) However, if one takes into account the presence of 1.9% of absorbed O_2 the determination is fairly correct.

1,2-*Bis-β-diethylaminoethenylcyclopentene* (**2b**). The reaction was effected on an analytical scale. Compound **1b** (0.2 g) was treated with 1 equivalent of *n*-BuLi under the same conditions as for **1a**, but the reaction vessel was then stoppered and stored in a freezer at −20° for 2 weeks. After the usual treatment the product was submitted to NMR spectroscopy.

In the same way compounds **2c** and **2d** were obtained.

1,2-*Bis-β-dimethylaminoethenylcyclopenten-4-ol* (**6**). Obtained as above with 2 equivalents of *n*-BuLi in order to take into account the OH group.

1,2-*Bis-β-dimethylaminoethenylcyclopenten-3-ol* (**7**). As above but after 6 hr the reaction was practically complete. The ^1H-NMR data of the above trienediamines are summarized in Table 1.

In the presence of Raney Ni, **2a** and **2b** absorb 6 mol of H_2 yielding *cis*-**3a**[16] and *cis*-**3b**, respectively, b.p. 150°/10 mm. (Found: C, 75.95; H, 13.46; N, 10.44. $C_{17}H_{36}N_2$ requires: C, 76.05; H, 13.52; N, 10.44%.)

1,2-*Bis-β-oximinoethylcyclopentene* (**8**). To the mixture arising from the treatment of 3.15 g (15 mmol) of **1a** with 14 ml of *n*-BuLi in hexane was added a soln of 6 g of hydroxylammonium chloride and 6 g of NaOAc in 10 ml of H_2O. The mixture was then heated in an oil bath and the solvent was distilled until the temp in the flask reached 85°. After cooling, H_2O was added and the resulting brownish ppt was filtered off under vacuum and washed several times with H_2O. Once dried it weighed 2 g. After crystallization from dilute EtOH, it had a m.p. of 153–154°. (Found: C, 59.30; H, 7.78; N, 15.30; O, 17.41. $C_9H_{14}N_2O_2$ requires: C, 59.32; H, 7.74; N, 15.37; O, 17.56%.)

1,2-*Bis-cyanomethylcyclopentene* (**10**). Compound **8** (0.55 g, 3 mmol) was refluxed for 5 min in 3 ml of Ac_2O. H_2O was then added. The mixture was extracted with Et_2O. The Et_2O soln was washed with 20% Na_2CO_3 and dried on K_2CO_3. After evaporation of the solvent the residue was distilled, b.p. (bath temp) 125°/10^{-4} mm. A solid (0.25 g) with m.p. 65° was thus obtained. (Found: C, 73.64; H, 6.91; N, 18.99; $C_9H_{10}N_2$ requires: C, 73.94; H, 6.90; N, 19.16%.)

1,2-*Bis-methoxycarbonylmethylcyclopentene* (**11**). Compound **10** (2 g, 13.7 mmol) was dissolved in 20 ml of abs MeOH. Dry HCl was bubbled into the soln with the exclusion of moisture until sat. After 1.5 hr refluxing, most of the solvent had been distilled off *in vacuo*. H_2O was then added. The product was extracted with Et_2O. The Et_2O soln was washed with H_2O and dried on $MgSO_4$. After evaporation of the Et_2O the product was distilled in a 'Kugelrohr' at 100° under 0.01 mm and 2.5 g (86%) of a liquid was obtained. (Found: C, 62.07; H, 7.69; O, 30.38; $C_{11}H_{16}O_4$ requires: C, 62.25; H, 7.60; O, 30.15%.)

1,2-*Bis-β-cyano-β-dimethylaminoethyl cyclopentene* (**12**). To the cooled mixture arising from the treatment of 4.45 g (21.7 mmol) of **1a** with 20 ml of *n*-BuLi soln, were added 6.5 g KCN dissolved in 12 ml of H_2O, followed by 10 ml of HOAc. The temp was then allowed to increase and when it reached 0°, 50 ml of a 20% soln of Na_2CO_3 was added dropwise. After extraction with CH_2Cl_2 and drying on K_2CO_3 5.3 g of product was obtained. Chromatography on 80 g of basic alumina, using Et_2O as eluent, afforded 4.5 g of a reddish partly crystallized mixture of the two diastereoisomers of **12** which was readily discoloured by stirring in Et_2O with charcoal. From a mixture of Et_2O and pentane 1.9 g of one diastereoisomer was obtained, m.p. 94°. (Found: C, 69.26; H, 9.23; N, 21.45; $C_{15}H_{24}N_4$ requires: C, 69.19; H, 9.29; N, 21.52%.) By concentrating the mother liquors, a low m.p. mixture of both forms was obtained and, from the remaining liquors, 1.2 g of the other diastereoisomer, m.p. 95°, was isolated, giving a depression when mixed with the former. (Found: C, 69.08; H, 9.38; N, 21.72%.)

1,2-*Bis-β-dimethylaminoethylcyclopentene* (**13**). Compound **12** (3.7 g, 14.2 mmol) in 20 ml of THF was added to 100 ml of liquid ammonia cooled to −50°. Na (2 g, 87 mmol) was added in small pieces at such a rate that decolorization occurred after each addition. At the end the soln remained dark. H_2O was then added and most of the ammonia was allowed to evaporate. Et_2O extraction, followed by drying on K_2CO_3 afforded, after distillation in a 'Kugelrohr' at 100°/0.05 mm, 2.6 g of a liquid. (Found: C, 74.00; H, 12.49; N, 13.19; $C_{13}H_{26}N_2$ requires: C, 74.22; H, 12.46; N, 13.32%.)

1,2 - *Bis* - *β* - *phenyl* - *β* - *dimethylaminoethylcyclopentene* (**14**). To a soln of PhMgBr prepared from 1.9 g (12 mmol) of bromobenzene in THF was added 1 g (3.85 mmol) of **12** (m.p. 94°). After refluxing for 2 hr and cooling, 10 ml of Et_2O conc NH_4Cl aq was added. Extraction with Et_2O and drying on K_2CO_3 afforded after 'Kugelrohr' distillation (b.p. 150–160°/0.005 mm) 1.15 g of a liquid.

The same reaction performed with the other diastereoisomer (m.p. 95°) gave the same mixture. (Found: C, 82.81; H, 9.50; N, 7.89; $C_{25}H_{34}N_2$ requires: C, 82.82; H, 9.45; N, 7.73%.)

1,2 - *Bis* - *β* - *dimethylamino* - 4 - *phenylbut* - 3 - *ynyl cyclopentene* (**15**). Similarly, with the Grignard obtained from 1.75 g (17.2 mmol) of phenylacetylene and 1 g (3.85 mmol) of **12**, 1.6 g of **15** was obtained, b.p. (bath temp) 160°/10^{-4} mm. (Found: C, 84.84; H, 8.39; N, 6.59; $C_{29}H_{34}N_2$ requires: C, 84.83; H, 8.35; N, 6.82%.)

1,2-*Bis-β-phenylethylcyclopentene* (**16**). Compound **14** (0.27 g, 0.75 mmol) was dissolved in 3 ml of Me_2CO and 0.5 g of MeI was added. After 3 hr the solvent was removed leaving 0.48 g of a thick paste. Liquid ammonia (10 ml) was poured into the flask under moisture exclusion and 0.3 g of Na was then added in small pieces as for **13**. After the addition of a few drops of H_2O, the ammonia was allowed to evaporate. On usual treatment, 0.17 g of a liquid was obtained, b.p. ('Kugelrohr') 150°/0.01 mm. (Found: C, 91.35; H, 8.90; $C_{21}H_{24}$ requires: C, 91.25; H, 8.75%.)

1,2-*Bis-β-phenylethenylcyclopentene* (**17**). To the methiodide prepared as above from 1.1 g (3 mmol) of **14**, 5 ml of MeOH was added followed by a soln of 1 g of KOH in 10 ml of H_2O. The mixture was heated on a water bath for 1.5 hr during which a solid appeared. After cooling, the solid was separated by filtration and washed with H_2O. Crystallization from Me_2CO–EtOH afforded 0.7 g of the triene, m.p. 146°. (Found: C, 92.23; H, 7.43; $C_{21}H_{20}$ requires: C, 92.60; H, 7.40%.)

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REFERENCES

[1] R. Epsztein and B. Herman, *J. Chem. Soc. Chem. Commun.* 1251 (1980).

[2] R. Epsztein and N. Le Goff, *Tetrahedron Lett.* 1965 (1981).

[3] E. Buncel, *Carbanions. Mechanistic and Isotopic Aspects*, p. 23. Elsevier, Amsterdam (1975).

[4] N. J. Leonard, P. D. Thomas and V. W. Gash, *J. Am. Chem. Soc.* **77**, 1552 (1955); N. J. Leonard and A. S. Hay, *Ibid.* **78**, 1984 (1956).

[5] D. S. Grierson, M. Harris and H. P. Husson, *Ibid.* **102**, 1064 (1980).

[6] C. Fabre and Z. Welvart, *Bull. Soc. Chim.* 2620 (1965).

[7] M. Bonin, J. R. Romero, D. S. Grierson and H. P. Husson, *Tetrahedron Lett.* 3369 (1982).

[8] G. Chauviere, B. Tchoubar and Z. Welvart, *Bull. Soc. Chim.* 1428 (1963).

[9] Z. Welvart, *Ibid.* 1653 (1961).

[10] C. R. Hauser, H. M. Taylor and T. G. Ledford, *J. Am. Chem. Soc.* **82**, 1786 (1960).

[11] C. R. Hauser and G. F. Morris, *J. Org. Chem.* **26**, 4740 (1961).

[12] G. Stork, A. A. Ozorio and A. Y. W. Leong, *Tetrahedron Lett.* 5175 (1978).

[13] E. Hebert, N. Maigrot and Z. Welvart, *Ibid.* 4683 (1983).

[14] J. P. Guermont, *C.R. Acad. Sci.* **237**, 1098 (1953).

[15] W. S. Johnson, T. M. Yarnell, R. F. Myers, D. R. Morton and S. G. Boots, *J. Org. Chem.* **45**, 1254 (1980).

[16] M. V. Mavrov, A. R. Derzhinskii and V. F. Kucherov, *Izv. Akad. Nauk SSSR, Ser. Khim.* 1460 (1965); M. V. Mavrov and V. F. Kucherov, *Ibid.* 1559 (1967); R. E. Dessy and S. A. Kandil, *J. Org. Chem.* **30**, 3857 (1965); *J. Am. Chem. Soc.* **88**, 3027 (1966).

[17] G. J. Karabatsos and R. A. Taller, *Tetrahedron* **24**, 3347 (1968).