Preparation and Properties of 1,6-Diazacyclodeca-3,8-diynes

Rolf Gleiter, ^{*}Joachim Ritter, Hermann Irngartinger and Jochen Lichtenthäler

Organisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, D-6900 Heidelberg (Germany)

Abstract: The preparation of four 1,6-diazacyclodeca-3,8-diynes is reported together with spectroscopic and structural properties (X-ray structure).

Ten-membered cyclic diynes have been synthesized in a remarkable number during the last decade^{1,2}. Because of their transannular interactions cyclodecadiynes have initiated a number of investigations concerning their reactivity and theoretical aspects¹⁻³. Nevertheless it seems surprising that - at least to our knowledge - the synthesis of diazacyclodecadiynes has not been reported.

We have prepared a series of N,N'-disubstituted diazacyclodecadiynes $(\underline{3a-d})$ in order to study their reactivity towards CpCoL (L= (CO)₂, COD) as well as their electronic properties. To accomplish this we devised a one pot reaction between the amine (<u>1</u>) and 1,4-dibromo-2-butyne⁴ (<u>2</u>) (Scheme 1). The yield of <u>3a-d</u> amounts to 5%. The most relevant spectroscopic data are given in Table 1.



a: $R = CH_3$ b: $R = C_2H_5$ c: $R = i-C_3H_7$ d: R = cyclohexyl

Scheme 1



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Other isolable products are the corresponding fifteen-membered trives $(\underline{4})$ and twenty-membered tetraynes $(\underline{5})$. As an example the spectroscopic data of $\underline{4b}$ and $\underline{5b}$ are shown in Table 2.



C(3')	- C(4)	1.190	N(1) - C(5)	1.466	C(2) - N(1) - C(5)	114.4°
C(2)	- C(3)	1.487	N(1) - C(6)	1.456	C(2) - C(3) - C(4')	169.8°
C(4)	- C(5)	1.484	C(3)C(4)	2.952	C(3') - C(4) - C(5)	170.8°
N(1)	- C(2)	1.464	N(1)N(1')	5.137		

Figure 1 Structure of <u>3a</u> according to an X-ray investigation with the most relevant interatomic distances (Å) and bond angles (e.s.d 0.001 - 0.002Å, 0.1°)⁶.

X-ray investigation on a single crystal of <u>3a</u> shows that both methyl

groups prefer an axial position in the chair conformation (Figure 1) in which the interaction between triple bonds and N-lone pairs presumably is minimal. Obviously there is no significant repulsion between the methyl group and the ring skeleton as is found in the case of N,N'-dimethyl-piperazine ($\underline{6}$) which exists predominantly in a bisequatorial conformation (in solution)⁵. Force field calculations (MMX) result in no distinct energy difference between bisequatorial and bisaxial conformation of <u>3a</u> whereas in the case of <u>6</u> a difference of 6 kcal/mol (MMX energy) is found.

Transannular interaction of both triple bonds leads to cisoid deformation of the alkyne moiety.

The chemistry of <u>3a-d</u> and other azacycloalkynes are currently under investigation.

Table 1 Most Relevant Analytical Data of the New Compounds <u>3a-d</u>.

- <u>3a</u> mp: 121°C ; ¹H-NMR (200 MHz, CDCl₃) δ: 3.51 (s, 8H), 2.55 (s, 6H); ¹³C-NMR (50.32 MHz, CDCl₃) δ: 82.19, 46.64, 39.88; MS m/e (relative intensity): 162 (M⁺, 16), 161 (M⁺- 1, 22), 42 (100), 106 (50), 119 (46), 118 (37), 51 (36), 120 (32), 134 (30); HR MS calcd. for C₁₀H₁₄N₂: 162.1156 found: 162.1136.
- <u>3b</u> mp: 58°C; ¹H-NMR (200 MHz, CDCl₃) δ: 3.55 (s, 8H), 2.85 (q, 4H), 1.09 (t, 6H); ¹³C-NMR (50.32 MHz, CDCl₃) δ: 82.15, 44.95, 44.27, 12.96; MS m/e (relative intensity): 190 (M⁺, 9), 189 (M⁺- 1, 40), 133 (100), 148 (74), 146 (70), 91 (60), 132 (56), 120 (53); HR MS calcd. for C₁₂H₁₈N₂: 190.1470 found: 190.1465.
- <u>3c</u> mp: $122 \,^{\circ}$ C ; ¹H-NMR (300 MHz, CDCl₃) δ : 3.60 (s, 8H), 3.32 (h, 2H) 1.11 (d, 12H); ¹³C-NMR (75.46 MHz, CDCl₃) δ : 82.72, 47.31, 43.30, 21.27; MS m/e (relative intensity): 218 (M⁺, 4), 217 (M⁺- 1, 9), 203 (100), 118 (47),147 (34), 41 (31), 120 (29), 91 (29) 161 (28), 160 (28), 43 (27), 132 (24), 146 (23), 94 (22); HR MS calcd. for $C_{10}H_{14}N_2$: 218.1783 found: 218.1796.
- <u>3d</u> mp: 175°C (decomp.); ¹H-NMR (300 MHz, CDCl₃) δ: 3.61 (s, 8H), 3.07 (m, 2H), 2.08 1.02 (m, 20H); ¹³C-NMR (75.46 MHz, CDCl₃) δ: 83.05, 54.88, 42.63, 30.79, 25.96, 25.30; MS m/e (relative intensity): 298 (M⁺, 10), 197 (M⁺ 1, 12), 41 (100), 55 (96), 106 (70), 200 (56), 93 (37), 187 (40), 118 (33); HR MS calcd. for C₂₀H₃₀N₂: 298.2409 found: 298.2399.

Table 2 Most Relevant Analytical Data of the New Compounds <u>4b</u> and <u>5b</u>.

<u>4b</u> ¹H-NMR (200 MHz, CDCl₃) δ : 3.55 (s, 12H), 2.61 (q, 6H), 1.07 (t, 9H); ¹³C-NMR (50.32 MHz, CDCl₃) δ : 80.46, 46.99, 43.05, 13.01; MS EI (CH₄, 40°C) m/e: 327 (M⁺+ 42), 316 (M⁺+ 31), 315 (M⁺+ 30), 287 (M⁺ + 2), 286 (M⁺+ 1), 285 (M⁺), 284 (M⁺- 1); DC (Al₂O₃/ cyclohexane/ ethylacetate 3:1) Rf= 0.27 . **<u>5b</u>** ¹**H-NMR** (200 MHz, CDCl₃) δ : 3.48 (s, 16H), 2.58 (q, 8H), 1.06 (t, 12H); ¹³**C-NMR** (50.32 MHz, CDCl₃) δ : 79.89, 46.80, 42.32, 12.81; **MS EI** (CH₄, 90 °C) **m/e**: 421 (M⁺+ 41), 410 (M⁺+ 30), 309 (M⁺+ 29), 382 (M⁺ + 2), 381 (M⁺+ 1), 380 (M⁺), 397 (M⁺- 1); **DC** (Al₂O₃/cyclohexane /ethylacetate 3:1) Rf= 0.15 .

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References

- See for example :^{(A}G. Eglinton, I.A. Lardy, R.A. Raphael, G.A. Sim, J. Chem. Soc. <u>1964</u>, 1154;^bF. Sondheimer, Y. Gaoni, J. Bregman, Tetrahedron Lett. <u>1960</u>, 25;^{(P.} Deslongchamps, S. Lamothe, H.-S. Lin, Can. J. Chem. <u>62</u> (1984), 2395; K.C. Nicolaou, G. Skokotas, P. Maligres, G. Zuccarello, E.J. Schweiger, K. Toshima, S. Wendeborn, Angew. Chem. <u>101</u> (1989) 1255, Angew. Chem. Int. Ed. Engl. <u>28</u> (1989) 1272.
- 2 R. Gleiter, M. Karcher, R. Jahn, H. Irngartinger, Chem. Ber. <u>121</u> (1988), 735;⁹R. Gleiter, D. Kratz, V. Schehlmann, Tetrahedron Lett. <u>29</u> (1988), 2813;¹C.R. Gleiter, S. Rittinger, Tetrahedron Lett. <u>29</u> (1988) 4529;³R. Gleiter, S. Rittinger, H. Langer, Chem. Ber. <u>124</u> (1991) 375; ⁴R. Gleiter, S. Rittinger, H. Irngartinger, Chem. Ber. <u>124</u> (1991) 365.
- 3 R. Gleiter, M. Karcher, W. Schäfer, Tetrahedron Lett. 28 (1985) 1635.
- 4 A. W. Johnson, J. Chem. Soc. <u>1946</u>, 1009.
- 5 F. Anet, I. Yavari, Tetrahedron Lett. 25 (1976), 2093.
- 6 Crystallographic data for <u>3a</u>: a = 6.135(1) Å, b = 10.072(1) Å, c = 7.583(1) Å, $\beta = 105.57(1)$ °. Space group $P2_1/c$; Z = 2; D_c= 1.19 g/cm³; V = 451.4(2) Å³. Data were collected on a ENRAF-NONIUS diffractometer (MoK_f radiation, graphite monochromator, ω -2 Θ scan) using a crystal of dimensions $0.40 \times 0.45 \times 0.5$ mm. Lorentz correction and polarisation correction have been applied. The structure was solved using MULTAN 11/82. 1071 independent reflections of which 839 were judged to be observed [I $\geq 2.5\sigma$ (I)]; R = 0.040. The position of the H atoms were calculated according to stereochemical requirements and refined isotropically. Complete structural data have been submitted to the **Cambridge Crystallographic Centre**.

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