Tetrahedron Letters,Vol.30,No.51,pp 7183-7186,1989
Printed in Great Britain

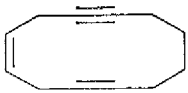
0040-4039/89 $3.00 + .00
Pergamon Press plc

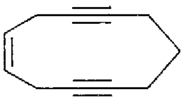
SYNTHESIS AND PROPERTIES OF MEDIUM SIZED NONCONJUGATED CARBOCYCLIC ENEDIYNES

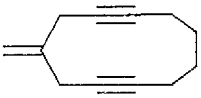
Rolf Gleiter* and Roland Merger
Institut für Organische Chemie der Universität Heidelberg
Im Neuenheimer Feld 270, D-6900 Heidelberg

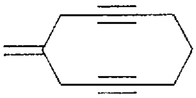
The syntheses and some properties of cyclododeca-4-ene-1,7-diyne(**1**), cycloundeca-4-ene-1,7-diyne (**2**), 4-methylene-cycloundeca-1,6-diyne (**3**), 4-methylene-cyclodeca-1,6-diyne (**4**) as well as their bis(dicobalthexacarbonyl) derivatives **11-14** are reported.

Initiated by questions concerning π/σ interactions we started to be interested in the properties of medium sized cyclic diacetylenes^{1}. These investigations led us to discover some unexpected pathways to cyclophanes^{2} and cage compounds^{3}. To extend these experiments we varied the structural parameters by adding an olefinic unit to the ring in such a way that a direct conjugation was prevented. In the following we report on the synthesis and some of the spectroscopic properties of the compounds **1-4**.


1


2

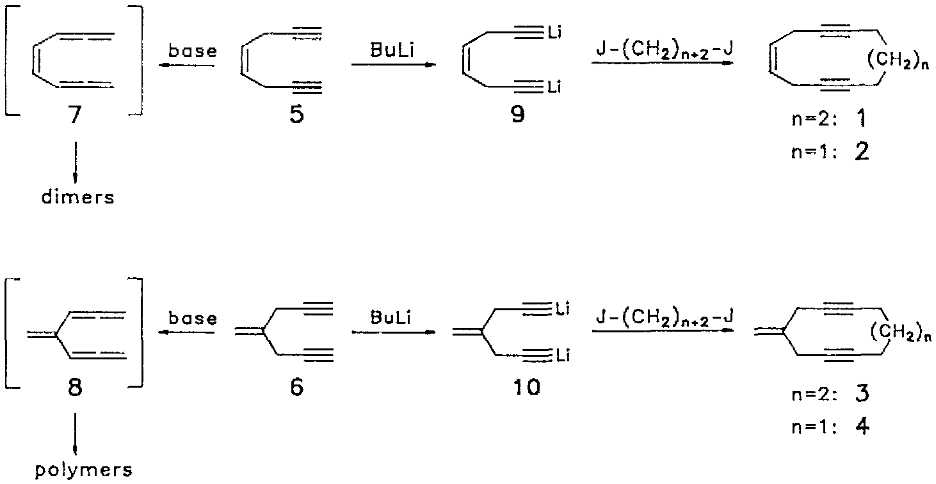

3


4

On treatment with strong bases, both (Z)-4-octene-1,7-diyne (**5**)^{4,5} and 4-methylene-hepta-1,6-diyne (**6**)^{6} readily isomerize via the corresponding bisallenes **7**^{4,5} and **8**^{7} to give dimeric or polymeric compounds. However, we found that preferential deprotonation at the acetylenic carbon atoms can be achieved by using BuLi as base in hexane/tetrahydrofuran as solvent. Subsequent alkylation^{8} of the dilithium salts **9** and **10** with either 1,4-diiodobutane or 1,3-diiodopropane at 60°C under an argon atmosphere yields 2-5% of the new enediynes **1**-**4** respectively (see Scheme 1). Isolation procedures involve flash chromatography (silica/CCl_4) followed by further purification of the crude products by treatment with an ethanolic solution of $AgNO_3$[9] in the case of **1**, or by distillation in the case of **3** (0.02 mbar/ca.75°C) and **4** (0.02 mbar/ca.85°C).

The most relevant spectroscopic data of compounds **1**-**4** are given in Table 1. ^{13}C NMR values of the acetylenic carbon atoms indicate considerable ring strain[10] particularly in the ten-membered ring **4**.

Scheme 1



The PE spectroscopic data of **1**-**4** reveal a similar splitting pattern as in the case of the parent ring systems. This is demonstrated in Figure 1 where we have compared the first PE bands of **2** with those of cycloundeca-1,6-diyne (**15**)[11] and **4** with cyclodeca-1,6-diyne (**16**)[12], respectively.

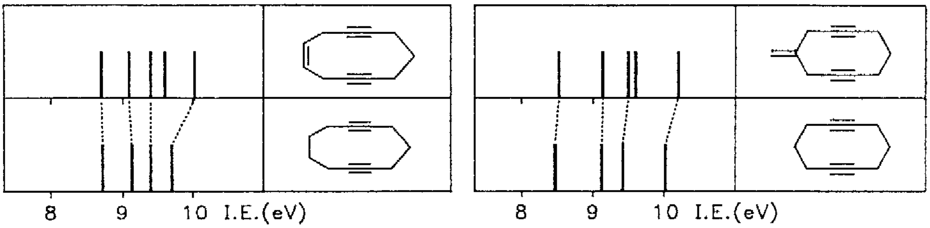
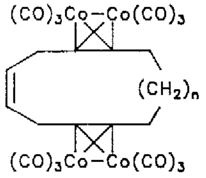


Fig. 1: Comparison between the first bands in the PE spectra of **2** and **15** (left) and **4** and **16** (right).

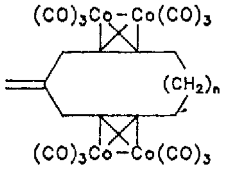
Selective reaction of the triple bonds with $Co_2(CO)_8$ (10% excess) in methylene chloride at room temperature affords the bis(dicobalthexacarbonyl)-complexes **11-14**, which are isolated in almost quantitative yield by chromatography on neutral alumina, using pentane to elute. These complexes are air-stable, dark-red solids, they gave correct elemental analyses and were characterized by their spectroscopic data (see Table 1).

The use of **7-10** as promising synthetic precursors and ligands will be detailed elsewhere.



n=2: 11

n=1: 12



n=2: 13

n=1: 14

Table 1 Selected Spectroscopic Data of **1-4** and **11-14**

1: ^{1}**H NMR** (300 MHz,$CDCl_3$) δ: 5.65 (t,2H); 2.85 (m,4H); 2.05 (m,4H); 1.6 (m,4H). ^{13}**C NMR** (75.46 MHz,$CDCl_3$) δ: 127.1 (d); 80.7 (s); 78.8 (s); 27.1 (t); 18.9 (t); 16.2 (t). **IR** cm^{-1}: 2272; 2220; 1634. $I_{v,j}$(eV): 9.10; 9.27; 9.88.

2: ^{1}**H NMR** (300 MHz,$CDCl_3$) δ: 5.7 (t,2H); 2.9 (m,4H); 2.2 (m,4H); 1.6 (m,2H). ^{13}**C NMR** (75.46 MHz,$CDCl_3$) δ: 127.5 (d); 81.1 (s); 79.8 (s); 25.9 (t); 18.9 (t); 16.2 (t). **IR** cm^{-1}: 2280; 2222; 1641. $I_{v,j}$(eV):

8.70; 9.09; 9.40; 9.60; 10.06.

3: **^{1}H NMR** (300 MHz,$CDCl_3$) δ: 4.9 (s,2H); 3.0 (t,4H); 2.1 (m,4H); 1,7 (m,4H). **^{13}C NMR** (75.46MHz,$CDCl_3$) δ: 141.4 (s); 114.5 (t); 82.8 (s); 78.6 (s); 27.5 (t); 27.2 (t); 20.3 (t). **IR** cm^{-1}: 2280; 2222; 1647. $I_{v,j}$(eV): 8.77; 9.07; 9.40; 9.53; 9.93.

4: **^{1}H NMR** (300 MHz,$CDCl_3$) δ: 4.9 (s,2H); 3.0 (t,4H); 2.3 (m,4H); 1.7 (m,2H). **^{13}C NMR** (75.46 MHz,$CDCl_3$) δ: 139.8 (s); 115.1 (t); 83.6 (s); 81.6 (s); 27.8 (t); 24.7 (t); 19.6 (t). **IR** cm^{-1}: 2218; 1641. $I_{v,j}$ (eV):8.53; 9.13; 9.48; 9.65; 10.23.

11: **^{1}H NMR** (300 MHz,$CDCl_3$) δ: 5.6 (br.,2H); 3.8 (br.,4H); 2.9 (br.,4H); 1.7 (br.,4H). **^{13}C NMR** (75.46 MHz,$CDCl_3$) δ: 200.7 (br); 128.1 (d); 99.2 (s); 96.4 (s); 34.3 (t); 34.2 (t); 30.6 (t).

12: **^{1}H NMR** (300 MHz,$CDCl_3$) δ: 5.7 (t,2H); 3.75 (d,4H); 3.1 (t,4H); 1.95 (m,2H). **^{13}C NMR** (75.46 MHz,$CDCl_3$) δ:200.5 (br.); 129.5 (d); 98.2 (s); 95.5 (s); 35.3 (t); 33.8 (t); 32.9 (t).

13: **^{1}H NMR** (300 MHz,$CDCl_3$) δ: 5.1 (br.,2H); 3.8 (br.,4H); 3.1 (br.,4H) 1.8 (br.,4H). **^{13}C NMR** (75.46MHz,$CDCl_3$) δ: 200.1 (br.); 144.3 (s); 115.9 (t); 97.5 (s); 94.2 (s); 41.8 (t); 33.7 (t); 30.1 (t).

14: **^{1}H NMR** (300 MHz,$CDCl_3$) δ: 5.05 (s,2H); 3.7 (s,4H); 3.0 (t,4H); 2.05 (m,2H). **^{13}C NMR** (75.46 MHz,$CDCl_3$) δ: 200.1 (br.); 144.8 (s); 116.1 (t); 95.8 (s); 94.9 (s); 41.5 (t); 32.1 (t); 31.4 (t).

Acknowledgement. We are grateful to the Deutsche Forschungsgemeinschaft (SFB 247), the Fonds der Chemischen Industrie and the BASF Aktiengesellschaft for financial support.

References

1 R. Gleiter, S. Rittinger, **Tetrahedron Lett.** 29, 4529 (1988); R. Gleiter, M. Karcher, D. Kratz, S. Rittinger, V. Schehlmann in: **"Organometallics in Organic Synthesis II"**, H. Werner, G. Erker Ed. Springer Verlag, Heidelberg 1989, 109 and references therein.

2 R. Gleiter, M. Karcher, M.L. Ziegler, B. Nuber, **Tetrahedron Lett.** 28, 195 (1987); R. Gleiter, M. Karcher, B. Nuber, M.L. Ziegler, **Angew. Chem.** 99, 805 (1987); **Angew. Chem. Int. Ed. Engl.** 26, 763 (1987).

3 R. Gleiter, M. Karcher, **Angew. Chem.** 100, 851 (1988); **Angew. Chem. Int. Ed. Engl.** 27, 840 (1988).

4 D.A. Ben-Efraim, F. Sondheimer, **Tetrahedron Lett.** 5, 313 (1963).

5 P. Müller, D. Rodriguez, **Helv. Chim. Acta** 68, 975 (1985).

6 B.E. Looker, F. Sondheimer, **Tetrahedron** 27, 2567 (1977).

7 H. Hopf, F. Lehrich, **Tetrahedron Lett.** 28, 2697 (1987).

8 A.Nissen, H.A.Staab, **Chem.Ber.** 104, 1191 (1971).

9 H.Fritz, E.Logemann, G.Schill, **Chem.Ber.** 109, 497 (1976).

10 H.Meier, H.Petersen, H.Kohlshorn, **Chem.Ber.** 113, 2398 (1980).

11 R. Gleiter, D. Kratz, V. Schehlmann, W. Schäfer, to be published.

12 R. Gleiter, M. Karcher, R. Jahn, H. Irngartinger, **Chem. Ber.** 121, 735 (1988).

(Received in Germany 9 October 1989)