Tetrahedron Letters, Vol.31, No.13, pp 1845-1848, 1990
Printed in Great Britain

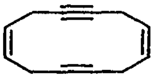
0040-4039/90 $3.00 + .00
Pergamon Press plc

SYNTHESIS AND PROPERTIES OF SKIPPED CYCLIC $C_{12}H_{12}$ DIENEDIYNES

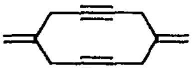
Rolf Gleiter* and Roland Merger
Institut für Organische Chemie der Universität Heidelberg
Im Neuenheimer Feld 270, D-6900 Heidelberg

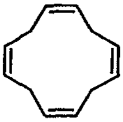
A simple synthetic procedure for the three skipped $C_{12}H_{12}$-dienediynes 1-3 and the corresponding all-cis tetraenes 4-6 is reported.

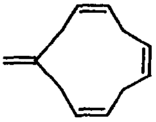
In "skipped" eneynes a methylene group separates a double bond from a triple bond. The three possible skipped cyclic dienediynes, cyclododeca-4,10-diene-1,7-diyne (1), 4-methylene-cycloundeca-9-ene-1,6-diyne (2) and 4,9-dimethylene-cyclodeca-1,6-diyne (3) are not only of interest as new $C_{12}H_{12}$-isomers, but also as starting materials for the corresponding tetraenes 4, 5 and 6. Unsuccessful attempts for the synthesis of 1 and 3 have been mentioned in the literature[1,2], whereas 4 has been prepared recently via a rather long route[3].

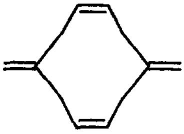

1


2


3

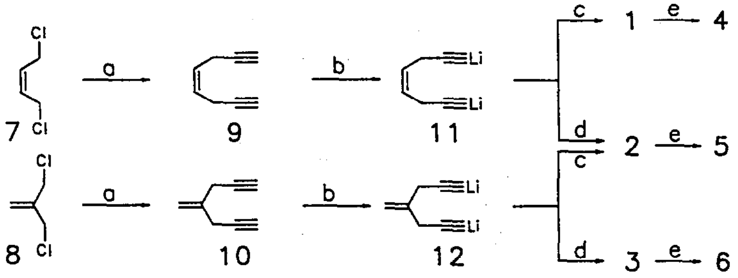

4


5


6

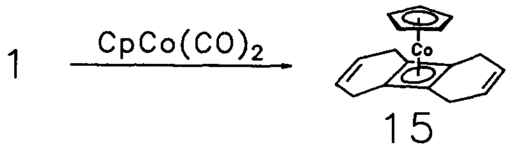
In this communication we report the simple preparation of compounds 1-6 in reasonable overall yields. We have also investigated the reaction of 1 with $CpCo(CO)_2$. Furthermore, spectroscopic properties concerning interactions of π-units in 3 will be commented on.

The preparation of 1-6 is outlined in Scheme 1. As we found recently[4], n-butyllithium readily reacts with (Z)-4-octene-1,7-diyne (9)[5,6] or 4-methylene-hepta-1,6-diyne (10)[2] to give the corresponding dilithium salts 11 and 12, with no formation of allenes[5-7] being observed. Both 11 and 12 could be alkylated with either (Z)-1,9-dibromo-2-butene (13)[8] or 3-iodo-2-iodomethyl-1-propene (14)[2] to give the new cyclic diynes 1-3 in 5% yield. Interestingly, there was no need for cuprous chloride, usually the essential catalyst for reactions of allylic halogenides with metal acetylides[9].



Scheme 1 Synthesis of 1-6: a) 6 equiv. $HC\equiv CMgCl$, 0.065 equiv. NaJ, 0.15 equiv. CuCl, THF, 60°C, 15h, 60%; b) 2.0 equiv. BuLi, THF, -78°C, 30 min; c) 1.0 equiv. (Z)-1,4-dibromo-2-butene (13), THF, -78°C → 60°C, 6h, 5%; d) 1.0 equiv. 3-iodo-2-iodomethyl-1-propene (14), THF, -78°C → 60°C, 6h, 5%; e) H_2, Lindlar-catalyst (10 mg per 100 mg of diyne), petrol ether, r.t., 5h, >70%.

In view of the low yields of the cyclization step, the syntheses of the acyclic diacetylenes 9 and 10 had to be improved. We found that the yield for the preparation of 9 from (Z)-1,4-dichloro-2-butene (7)[10] can be raised from 20%[6] to 60% when the substitution is carried out with ethynylmagnesium chloride[11] instead of ethynylmagnesium bromide. Equally, 10 can be made directly from 3-chloro-2-chloromethyl-1-propene (8) in 60% yield, thus simplifying the route to 10 by avoiding the intermediate preparation of the strongly lachrymatory 14[2]. Hydrogenation of 1-3 in petrol ether under the influence of Lindlar catalyst affords the corresponding tetraenes 4 to 6 in high yields, the promising chemistry of which can now be explored. Treatment of 1 with $CpCo(CO)_2$ leads to the intramolecular cyclobutadiene complex 15, a product which is anticipated considering the analogous reaction of cyclododeca-1,7-diyne[12,13] (see Scheme 2).



Scheme 2 Reaction of 1 with $CpCo(CO)_2$. Conditions: 1.1 equiv. $CpCo(CO)_2$, refluxing n-octane, 24h, 40%.

The most relevant spectroscopic data of 1-3, 5, 6 and 15 are given in Table 1. The ^{13}C-NMR-shift of δ=82.1 ppm for the quarternary carbon atoms in 1 indicates considerable deformation of the acetylenic bond angles[14] as a result of repulsion between the two triple bonds. This is confirmed by the PE-spectrum of 1, which reveals a splitting pattern related to that of the parent ring compound, cyclodeca-1,6-diyne 16[15], thus giving evidence of strong interactions between the π-orbitals of 1.

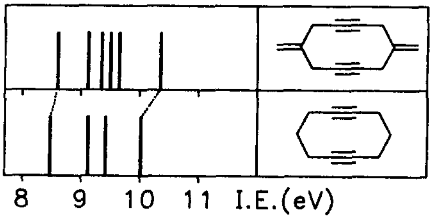


Figure 1: Comparison between the first bands in the PE spectra of 1 and 16.

Further investigations concerning the organic and organometallic chemistry of 1-6 and 15 are in progress.

Acknowledgements. We are grateful to the Deutsche Forschungsgemeinschaft (SFB 247), the Fonds der Chemischen Industrie and the BASF-Aktiengesellschaft for financial support. R.M. thanks the Studienstiftung des Deutschen Volkes for a Ph.D. grant.

Table 1 Selected Spectroscopic Data of 1-6 and 15.

1 ^{1}**HNMR** (300 MHz, $CDCl_3$) δ: 5.68 (t,4H), 2.87 (d,8H); ^{13}**C-NMR** (75.46 MHz, $CDCl_3$) δ: 127.24 (d), 78.38 (s), 17.24 (t); IR(cm^{-1}): 2274, 2210, 1643; $I_{v,j}$ (eV): 9.0, 10.0.

2 ^{1}**H-NMR** (300 MHz, $CDCl_3$) δ: 5.75 (t,2H), 4.87 (s,2H), 2.95 (m,2H), 2.88 (m,2H); ^{13}**C-NMR** (75.46 MHz, $CDCl_3$) δ: 140.23 (s), 127.48 (d), 115.22 (t), 27.57 (t), 17.09 (t); IR (cm^{-1}) : 2274, 2212, 1638; $I_{v,j}$ (eV): 8.70, 9.08, 9.30, 9.48, 9.75, 10.07.

3 ^{1}**H-NMR** (300 MHz, $CDCl_3$) δ: 4.9 (s,4H), 3.0 (s,8H); ^{13}**C-NMR** (75.46 MHz, $CDCl_3$) δ: 138.9 (s), 115.5 (t), 82.1 (s), 27.77 (t);IR(cm^{-1}): 2276, 2210, 1640; $I_{v,j}$ (eV): 8.60, 9.12, 9.35, 9.50, 9,65, 10.35.

5 ^{1}**H-NMR** (300 MHz, $CDCl_3$) δ: 5.69 (m,2H), 5.32 (m,4H), 4.80 (s,2H), 2.87 (m,8H); ^{13}**C-NMR** (75.46 MHz, $CDCl_3$) δ: 147.66 (s), 129.11 (d), 128.14 (d), 127.98 (d), 111.73 (t), 39.73 (t), 26.90 (t); IR (cm^{-1}):1634.

6 ^{1}**H-NMR** (300 MHz, $CDCl_3$,20°C) δ: 5.35 (m,4H), 4.84 (s,4H), 2.82 (br.8H); ^{1}**H-NMR** (200 MHz CD_2Cl_2,-50°C) δ: 5.29 (m,4H), 4.80 (s,4H), 3.07 (t,4H), 2.44 (d,4H); ^{13}**C-NMR** (75.46 MHz, $CDCl_3$) δ: 146.99 (s), 129.15 (d), 112.16 (t), 34.16 (t); IR(cm^{-1}): 1640.

15 ^{1}**H-NMR** (300 MHz, C_6D_6) δ: 5.63 (s,4H), 4.56(s,5H), 2.83 (d,4H), 2.56 (d,4H); ^{13}**C-NMR** (75.46 MHz, C_6D_6) δ: 124.25 (d), 81.16 (d), 71.79 (s), 24.50 (t); IR(cm^{-1}) : 3016 (m), 2808 (m), 1634 (w), 1420 (s), 1123 (m), 801 (s); UV (n-pentane) $\lambda_{max}(\lg\epsilon)$: 202 (2.98), 265 (3.06).

References

1 M. Brudermüller, H. Musso, **Chem.Ber.** 121 (1988) 2255; M. Brudermüller, H. Musso, A. Wegner **ibid.** 121 (1988) 2239.

2 B.E. Looker, F. Sondheimer, **Tetrahedron** 27 (1971) 2567.

3 M. Brudermüller, H. Musso, **Angew. Chem.** 100 (1988) 267.

4 R. Gleiter, R. Merger, **Tetrahedron Lett.** 30 (1989) 7183.

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

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

7 H. Hopf, F. Lehrich, **Tetrahedron Lett.** 281 (1987) 2697.

8 C. Prevost, A. Valette, **Compt. rend.** 222 (1946) 327.

9 L. Brandsma "Preparative Acetylenic Chemistry", 2nd Ed., Elsevier, Amsterdam, (1988), p. 223; V. Jäger, "Alkine", in: Houben-Weyl "Methoden der Organischen Chemie", 4th Ed., V/2a, Stuttgart (1977), p.273.

10 7 was prepared as described in: L. Brandsma "Preparative Acetylenic Chemistry", 1st Ed., Elsevier, Amsterdam (1971), p.187.

11 E. Vedejs (Ed.), **Organic Syntheses** 65 (1987) 61.

12 R.B. King, A. Efraty, **J. Am. Chem. Soc.** 992 (1970) 6071.

13 R. Gleiter, M. Karcher, D. Kratz, S. Rittinger, V. Schehlmann in H. Werner, G. Erker (Edit.):"Organometallics in Organic Synthesis 2", Springer Verlag, Berlin, Heidelberg 1989 p. 109 f.

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

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

(Received in Germany 2 February 1990)