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SYNTHESIS OF CpCo-COMPLEXED α-PYRANS VIA AN INTRAMOLECULAR [2+2+2] CYCLOADDITION

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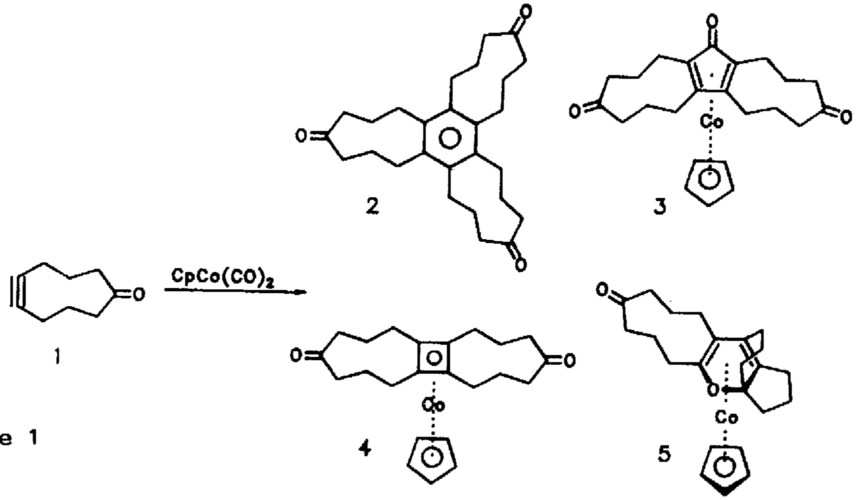
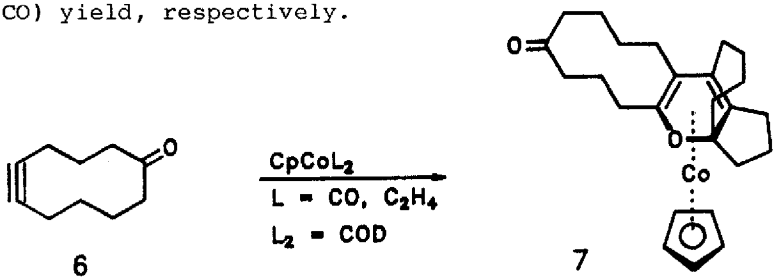
Abstract - Treatment of 5-cyclononynone (**1**), 5-cyclodecynone (**6**), dodecanal-1,7-diyne (**10**) and tridecanal-1,7-diyne (**11**) with CpCoL$_2$ (L = CO, C_2H_4, L_2 = COD) yields the polycyclic α-pyrans **5**, **7**, **12** and **13** complexed by a CpCo unit.

During our studies on the metal assisted di- and trimerization of 5-cyclononynone (**1**)[1] we found as the main product the benzene derivative **2** and, as expected, the side products **3** and **4**.[2] The isolation of the highly strained α-pyran **5**, whose structure was confirmed by X-ray crystallography[3] was surprising to us (see **Scheme 1**). First because we did not expect the carbonyl function to be affected by the oligomerization catalyst CpCoL$_2$, and secondly, no case of a metal assisted [2+2+2] cycloaddition[4] involving a C=O double bond had been reported when we started our investigations.[5]



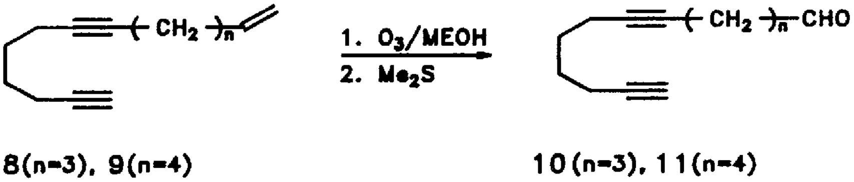
Scheme 1

To test whether other cyclic ynones react in an analogous fashion, we treated 5-cyclodecynone[6] (**6**) with $CpCoL_2$ to give **7** in 25% ($L=C_2H_4$) or 5% (L=CO) yield, respectively.



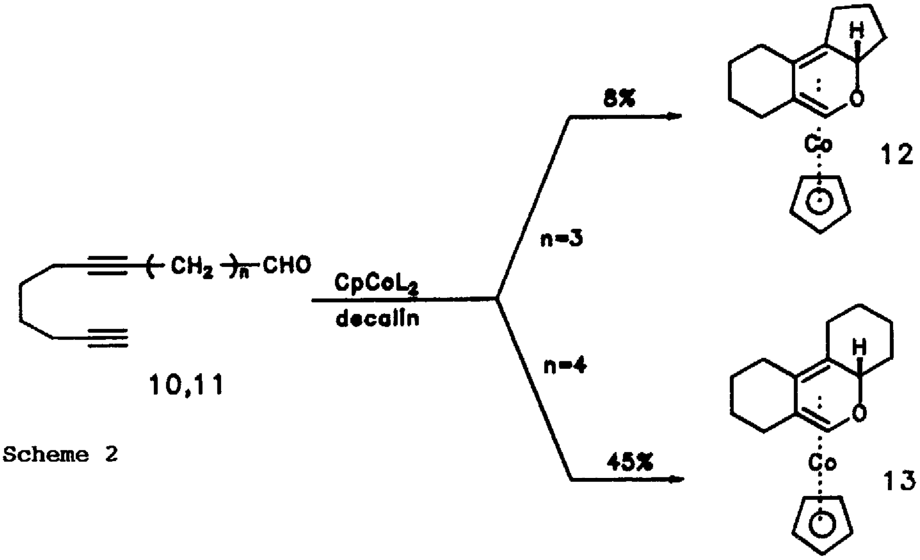
(1)

In contrast to the above examples, where the pyran ring is constructed of two ynones, we decided to perform the [2+2+2] cyclization in a completely intramolecular manner. Therefore we synthesized the olefins **8** and **9** according to Sternberg and Vollhardt.[7] Ozonolysis of these compounds with subsequent reductive workup procedure gave the aldehydes **10** and **11** in about 50% yield.



(2)

The cyclization of **10** and **11** with $CpCo(CO)_2$ or CpCo(COD) (**Scheme 2**)



Scheme 2

was carried out at 140-150°C in decalin to obtain the CpCo-complexed tricyclic α-pyrans **12** and **13**. An X-ray investigation on **13** revealed that the sp^3 hydrogen at the pyran ring is **anti** to the metal fragment.[3] From the similarity of the spectroscopic data of **12** and **13** we conclude that both compounds have the same configuration. The most relevant analytical data of **10**, **11** as well as **5**, **7**, **12** and **13** are listed in **Table 1**.[8]

Table 1 Most Characteristic Analytical Data of 5, **7** and **10** - **13** [8].

5 **mp**: 147°C; **^{1}H NMR** ($CDCl_3$, 300 MHz) δ: 4.51(s,5H), 2.90-3.04(m,1H), 2.60-2.90(m,4H), 1.35-2.34(m,18H), 0.84-1.00(m,1H); **^{13}C NMR**($CDCl_3$, 75.46 MHz) δ: 215.3, 113.6, 90.3, 88.6, 82.8(Cp), 69.1, 58.3, 41.1, 38.9(2C), 38.4, 34.2, 32.4, 29.4, 28.8, 25.5, 25.0, 24.0, 21.1; **IR**(KBr)[cm^{-1}] 2912, 1700, 1415; **UV**(pentane) λ_{max}(lg ε)[nm]: 395(2.9), 325(3.4), 278(3.9), 227(4.3).

7 **mp**: 123-125°C; **^{1}H NMR** ($CDCl_3$, 300 MHz) δ: 4.45(s,5H), 1.28-2.90(m,27H); 1.09-1.17(m,1H); **^{13}C NMR** ($CDCl_3$, 75.46 MHz) δ: 213.7, 111.5, 87.0, 84.0, 82.9, 69.8, 64.5, 44.3, 40.4, 38.8(2C), 33.2, 32.9,28.0, 27.8, 26.6, 24.8, 24.3, 24.2, 22.7, 22.0; **IR**(KBr)[cm^{-1}]: 2942, 1701, 1418; **UV**(pentane) λ_{max}(lgε) [nm]: 370(2.9), 300(3.6); 273(3.9), 218(4.3).

12 **mp**: 80-81°C; **^{1}H NMR** ($CDCl_3$, 300 MHz) δ: 5.45(s,1H), 4.62(s,5H), 1.56-2.74(m,15H); **^{13}C NMR** ($CDCl_3$, 75.46 MHz) δ: 91.9, 90.6, 82.0, 77.3, 75.9, 72.1, 32.7, 28.6, 26.0, 25.7, 23.0, 22.4, 20.0; **IR**(KBr)[cm^{-1}]: 3008, 2916, 1435; **UV**(pentane) λ_{max} (lg ε) [nm]: 372(2.8), 297(3.6), 266(4.0), 197(4.3)

13 **mp**: 75 - 76°C; **^{1}H NMR** ($CDCl_3$, 200 MHz) δ: 5.41(s,1H), 4.71(s,5H), 2.15-2.65(m,3H), 1.00-2.65(m,14H); **^{13}C NMR** ($CDCl_3$, 50.32 MHz) δ: 91.4, 90.5, 82.0, 79.6, 76.0, 68.4, 34.2, 31.7, 26.9, 26.3, 25.4, 24.7 24.0, 22.7; **IR**(KBr)[cm^{-1}]: 3002, 2920, 1434; **UV**(pentane) λ_{max}(lgε) [nm]: 377(2.8), 297(3.6), 265(4.1), 197(4.3).

10 colorless oil; ^{1}**H NMR** ($CDCl_3$, 300 MHz) δ: 9.81(t,1H), 2.47(dt, 2H), 2.10-2.30(m,6H), 1.97(t,1H), 1.45-1.86(m,6H); ^{13}**C NMR** ($CDCl_3$, 75.46 MHz) δ: 202 1, 84.0 79.0, 78.8, 68.3, 42.6 27.8, 27.7, 23.8, 21.3, 18.0, 17.8; **IR**(film)[cm^{-1}]: 3286, 2936, 2110, 1706, 1430.

11 colorless oil; ^{1}**H NMR** ($CDCl_3$, 200 MHz) δ: 9.66(t,1H), 2.36(dt, 2H), 2.04-2.14(m,6H), 1.87(t,1H), 1.37-1.67(m,8H); ^{13}**C NMR** ($CDCl_3$, 50.32 MHz) δ: 202.8, 84.6, 80.6, 80.2, 69.0, 43.8, 28.9 28.4, 28.0, 21.7, 18.9, 18.7, 18.4; **IR**(film)[cm^{-1}]: 3282, 2930, 2108,1721,1429.

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