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Deltacyclene formation catalysed by cationic Co(II) complexes

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Abstract

Alkynes and norbornadiene can be codimerized in a [2 + 2 + 2] Homo–Diels–Alder reaction, yielding deltacyclenes. Instead of reduced Co species as used in former cases, Co(II)-complexes activated with Lewis acids such as ZnI_2 or $ZnCl_2$ are used to obtain the same products. The $[CoI(PPh_3)_2]^+$ cation appears to be the catalytically active compound.

Keywords: Deltacyclenes; Homo-Diels-Alder-reaction; Cationic Co(II) catalysts; Catalysis

1. Introduction

Homo–Diels–Alder reactions are a special case of [2 + 2 + 2] cycloadditions. Over the past few years the catalytic addition of alkynes to norbornadiene (nbd) has received increasing interest, not least of all because, by utilizing optically active catalysts, enantiomerically pure deltacyclenes were made accessible [1–3]. Although electron-deficient alkynes give [2 + 2 + 2] cycloadducts with nbd spontaneously [4], alkynes RCCH without strong electron-withdrawing groups do not react without the help of a metal catalyst. The nature of the catalyst has a distinct influence on the product distribution; ruthenium complexes such as $[RuH_2(PPh_3)_4]$ or $[Cp^*RuCl(cod)]$ lead to a [2 + 2] cycloaddition of alkynes to a single double bond of nbd [5,6] whereas the use of a nickel catalyst, depending on the alkyne used, results in [2 + 2], [2 + 2 + 2] and even [2 + 2 + 2 + 2] cycloadducts [7,8]. A cobalt catalyst for the synthesis of deltacyclenes, prepared through the reduction of $Co(acac)_3$ with an excess amount of Et_2AlCl in the presence of DPPE was found by Lyons et al. [9]. The deltacyclenes are formed with selectivities between 16 and 95%; byproducts are nbd homodimers. Over the following years the experimental procedure for this cycloaddition was improved [10], and an intramolecular variant was published in 1992 [11]. Nevertheless, the use of organoaluminium compounds for the reduction of the cobalt precursor made it difficult to use sensitively functionalized alkynes such as propargyl ether which led to only moderate yields in the experiments described above. This problem however, has recently been solved through the utilization of zinc dust as a reducing agent [3,12].

Despite the advances made over the last years, the nature of the catalytically active species still remains unknown. In the cobalt catalysts reported until now, a Co(II) or Co(III) salt is reduced to a Co(I) or even Co(0) species by an aluminium organic compound or by zinc. We have now found that a catalytically active system for the deltacyclene formation from nbd (**1**) and 1-alkynes (**2**) can be developed by just adding the appropriate Lewis acid such as ZnI_2 or $ZnCl_2$ to the Co(II) precatalyst $[(Ph_3P)_2CoI_2]$ [12]; no reduction is involved in the preparation of this new active cobalt catalyst. Some preliminary results produced with this new catalytic system are reported herein.

2. Results

In one of the above-mentioned publications, Cheng and coworkers [12] reported that nbd (**1**) and 1-hexyne (**2a**) codimerize in CH_2Cl_2 in the presence of an in situ catalyst prepared from CoI_2, Ph_3P and Zn in the molar ratio 1 : 2 : 10 to give after 0.5 h at 19°C the deltacyclene **3a** with a 93% yield. In our work, this procedure leads after 1 h at 22°C to **3a** with a 89% yield. When we used $[(Ph_3P)_2CoI_2]$ activated by a fivefold excess of ZnI_2 as the catalyst under otherwise identical conditions, **3a** is

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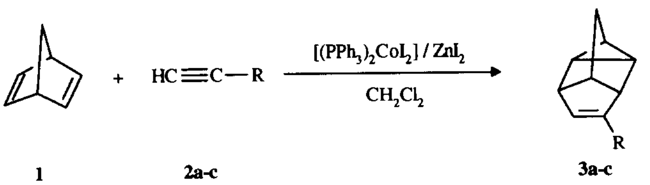


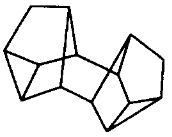
a : R = nC_4H_9 84 % yield
b : R = Ph 87 % yield
c : R = $SiMe_3$ 57 % yield

formed with a 84% yield together with 7% of a codimer of an unknown structure. We believe that this codimer is formed by insertion of **1** into the acetylenic CH bond of **2a** as observed by Lautens and Coudder [10]. Substitution of the Lewis acid ZnI_2 by $ZnCl_2$ in this new catalytic systems gives a more active catalyst with a reduced lifetime. Now, the codimerization between **1** and **2a** at 22°C is strongly exothermic, but the reaction stops at a conversion of 73% of **1** and **2a** to **3a**:
Under the influence of the catalyst $(Ph_3P)_2CoI_2 : ZnI_2$ in the ratio 1 : 5, other 1-alkynes such as phenylacetylene **2b** or trimethylsilylacetylene **2c** react in the same manner, whereas with disubstituted acetylenes, e.g tolane, no cycloadditions could be observed. Compounds **2b** and **2c** are less reactive than **2a**. Thus the codimerization of **2b** with **1** is completed after stirring at 22°C for 12 h. Compound **3b** could be isolated as the only reaction product with a 87% yield. With **2c** the reaction mixture must be heated to 40°C for 6 h to be completed. Under this condition the codimer **3c** is formed with a 57% yield together with the nbd homodimer **4**, which could be isolated with a yield of 24%:

These results clearly indicate that Co(II) salts do not necessarily have to be reduced to give an active catalyst for reactions of this kind. We believe that the active catalyst in these new cobalt(II) systems is a cationic species of the following compositions:

$$[(Ph_3P)_2CoI]^+ [ZnI_3]^- \text{ or } [(Ph_3P)_2Co]^{2+} [ZnI_4]^{2-}$$

which are able to catalyse the described codimerizations in the same manner as, for example, Co(I) or Co(0) species which are obtained by treating $[(Ph_3P)_2CoI_2]$ with zinc powder.



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3. Experimental part

3.1. Deltacyclene 3a

A mixture of CoI_2 (100 mg, 0.32 mmol) and PPh_3 (170 mg, 0.64 mmol) is dissolved in CH_2Cl_2 (20 ml). After stirring for 15 min, ZnI_2 (511 mg, 1.60 mmol) is added and the whole mixture again stirred for 15 min. Into this brown-coloured suspension nbd (**1**) (1.47 g, 16 mmol) and 1-hexene (**2a**) (1.31 g, 16 mmol) is pipetted at 22°C and the reaction mixture is stirred for 1 h. After that the reaction is completed (gas chromalography (GC) control), the mixture is filtered through a Florisil column in order to separate the catalyst and the column is washed with CH_2Cl_2 (50 ml). From the filtrate the solvent is distilled off to generate a yellow viscous liquid (2.33 g) of the composition (GC) 1% of CH_2Cl_2, 3% of **2a**, 5% of **1**, 84% of **3a** and 7% isomer of **3a** (M^+ found by GC–Mass Spectroscopy (MS) combination 174), from which pure **3a** (1.86 g (69%)) is separated by preparative GC as a slightly viscous colorless liquid; spectra obtained by (MS), ^1H NMR and ^{13}C NMR are identical with those of authentic material [10–13].

3.2. Deltacyclene 3b

Compound **3b** has been prepared in an analogous manner to the procedure described for **3a**, with the exception that the reaction mixture must be stirred at 22°C for 12 h. In the presence of 2 mol.% of the above mentioned catalyst, one isolates from **1** (1.61 g, 17.5 mmol) and **2b** (1.78 g, 17.5 mmol), **3a** (2.95 g (87%)) as a viscous colorless oil; spectra obtained by MS, ^1H NMR and ^{13}C NMR were identical with those of an authentic sample [10,13].

3.3. Deltacyclene 3c

A mixture of 2 mol.% of the above mentioned catalyst, **1** (1.47 g, 16 mmol) and **2c** (1.57 g, 16 mmol) in CH_2Cl_2 (20 ml) is heated to reflux for 6 h. After the usual work-up procedure, one obtains 2.53 g of a slightly yellow liquid of the composition (GC) 17% of **2c**, 69% of **3c** (57% calculated yield) and 14% of **4** (24% calculated yield). Through preparative GC, **3c** (0.83 g) and **4** (0.2 g) are obtained in pure form; spectra obtained by MS ^1H NMR and ^{13}C NMR were identical with those of an authentic sample [10,13].

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