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## First Examples of Cobalt-Mediated Formal Alder Ene Reaction of Allenynes.

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Abstract: CpCo(CO)<sub>2</sub> catalyzes the Alder ene reaction of allenynes I to afford six-membered carbocycles in a totally regioselective manner through, presumably, η<sup>3</sup>-allyl hydride complexes mechanism. Copyright © 1996 Published by Elsevier Science Ltd

Despite its potential usefulness, the Alder ene reaction has been limited in synthesis because of the need for extreme reaction conditions or strict structural requirements. Transition-metal-catalyzed versions have provided an opportunity to overcome these limitations. Though some intramolecular formal Alder ene reactions - the latter being cycloisomerizations - of enynes have been reported, as far as we are aware no metal complex catalyzed ene reactions with allenynes have been recorded in the literature. However, allenes have occasionnally been used in ene reactions of enallenes either as enophile in thermal or Lewis acid catalyzed reactions or as ene component when other reactions are not possible. Despite the fact that allenes are known to be good ligands in organometallic complexes, only few examples involving allenes or allenyl species in transition-metal-catalyzed cyclizations or metallo-ene-reactions.

Recently, we have shown that allenes are new and excellent partners in cobalt-mediated [2+2+2] cycloaddition reactions. While we were exploring the scope of the allenediynes cyclizations, we disclosed that cobalt (I) complexes could catalyze a formal Aider ene reaction of allenynes I (Scheme 1). Here, we describe the preliminary results of this cyclization that directly affords in a totally regionselective manner, six-membered carbocycles which are otherwise difficult to obtain.

 $a: R = (H_2C)_3 - SiMe_3$ 

**b** : R ≈ H

Scheme 1

The allenynes 1 were readily prepared following scheme 2. Double alkylation of the sodium derivative of dimethylmalonate with propargyl bromide and then 1-methanesulfonyloxy-9-trimethylsilylnon-2,8-diyne or propargyl bromide provided the compounds 4a and 4b respectively. Reduction of the ester functions followed by acid catalyzed protection with acetone furnished the acetonides 5. Condensation of their lithium acetylide on propionaldehyde gave the alcohols 6. Heterocuprate mediated reactions 12 from the corresponding mesylates 7 afforded the allenynes 1a and after subsequent silylation 1b.

(a) 4a: (i) NaH, BrCH<sub>2</sub>C=CH, THF, r. t., 50% (ii) NaH, MsOCH<sub>2</sub>C=C(CH<sub>2</sub>)<sub>3</sub>C=CSiMe<sub>3</sub>, 73%; 4b: NaH, BrCH<sub>2</sub>C=CH (2 eq.), THF,  $\Delta$ , 98%. (b) (i) LiAlH<sub>4</sub>, Et<sub>2</sub>O, r. t., 1h (ii) cat. PTSA, acetone, 5a: 73%; 5b: 53%. (c) n-BuLi (1.1 eq.), THF, - 78°C, C<sub>3</sub>H<sub>6</sub>O, 6a: 92%; 6b: 33%. (d) (i) CH<sub>3</sub>SO<sub>2</sub>Cl, - 30°C, CH<sub>2</sub>Cl<sub>2</sub>, DMAP, Et<sub>3</sub>N, 7a, 7b: quant. (e) t-BuCuCNLi, THF, - 78°C, 1a: 50%. (f) n-BuLi, THF, - 78°C, CISiMe<sub>3</sub>, 1b: 68%.

## Scheme 2

When the allenyne 1a was exposed to a stoichiometric amount of  $(\eta^5$ -cyclopentadienyl) cobalt dicarbonyl  $[CpCo(CO)_2]$  under irradiation in refluxing xylenes for 3h, a 2:3 mixture of adduct 2a and  $(\eta^4$ -cyclohexadiene) cobalt complexes 3a was obtained in 49 % yield. Adducts 2a and 3a consisted themselves as a 7:3 mixture of E and E isomers. No traces of E cycloadducts were observed meaning that the silylated triple bond has not reacted in the overall process. Similarly, exposure of the allenyne 1b to E to E and 3b in 60 % yield. Control experiments showed that allenynes 1 were totally recovered in boiling xylenes with or without irradiation, indicating the crucial role of the cobalt complex.

Although the course of the cyclization of 1 could not be ascertained, the formation of 2 and 3 appears to implicate  $\eta^3$ -allyl hydride complexes (Scheme 3). Indeed, after coordination of the allenyne with the cobalt complex, the next step could be the oxidative formation of the  $\eta^3$ -allyl hydride complex 9. Successive alkyne insertion into the cobalt-hydride bond and reductive elimination would afford 2. We anticipated that the formation of the  $(\eta^4$ -cyclohexadiene) cobalt complexes 3 could be the result of a cobalt-mediated migration of the double

bond via the allyl hydride 11. To our knowledge, no examples involving the formation of such hydrides with allenes have been reported, however this type of intermediates has been invoked to explain the isomerization of double bonds in presence of cobalt (I) complexes.<sup>14</sup>

In summary, these preliminary results provide a new and efficient catalysis for effecting the Alder ene reaction of unactivated allenes and alkynes. This process allows for the construction of six-membered carbocycles which are quite difficult to attain through the cycloisomerization of 1,7 enynes.<sup>15</sup>

Further extensive studies aimed at defining the scope, the limitations and the mechanism of this reaction are currently under active progress in our laboratories.

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- 13. Typical procedure for the cyclization of 1.  $CpCo(CO)_2$  (1 mmol; 125  $\mu L$ ) was added to a refluxing solution of 1 (1 mmol) in xylenes (10 mL) degassed by three freeze-pump-thaw cycles and was irradiated (light from a projector lamp; ELW, 300W, 70% of its power). The reaction was monitored by TLC and after completion, the solvent was removed in vacuo. The residue was purified by flash chromatography (petroleum ether : ether = 9 : 1) to afford the adducts 2 and 3. (E)-2b :  ${}^{1}$ H-NMR (400MHz,  $C_{\kappa}D_{\kappa}$ )  $\delta$  6.32 (d, J = 16.0 Hz, 1H), 5.76 (dq, J = 16.0, 6.6 Hz, 1H), 4.52 (s, 5H), 3.97 (AB, 2H), 3.45 (AB, 2H), 2.51(s, 1H), 2.31 (d, J = 13.9 Hz, 1H), 1.88 (d, J = 13.9 Hz, 1H), 1.67 (d, J = 6.6 Hz, 3H), 1.49 (s, 6H), 1.15 (s, 9H), 0.91 (d, J = 13.7 Hz, 1H), 0.17 (d, J = 13.7 Hz), 0.04 (s, 9H);  $^{13}$ C-NMR (50 MHz,  $C_6D_6$ ) δ 134.3, 132.3, 98.3, 94.6, 92.8, 82.9 (5C), 75.8, 72.3, 72.2, 56.2, 41.8, 38.7, 36.3, 31.9 (3C), 28.1, 25.9, 22.3, 19.3, 0.3 (3C), (Z)-2b; <sup>1</sup>H-NMR (400MHz,  $C_6D_6$ )  $\delta$  6.68 (d, J = 11.0 Hz, 1H), 5.49 (dt, J = 11.0 Hz, 1H) 11.0, 6.9 Hz, 1H), 4.48 (s, 5H), 3.97 (AB, 2H), 3.45 (AB, 2H), 2.78 (s, 1H), 2.16 (d, J = 16.0 Hz, 1H), 1.78 (d, J = 14.1 Hz, 1H), 1.67 (t, J = 6.9 Hz, 3H), 1.50 (s, 6H), 1.15 (s, 9H), 0.87 (d, J = 16.0 Hz, 1H), 0.17 (d, J = 14.1 Hz, 1H), 0.05 (s, 9H); <sup>13</sup>C-NMR (50 MHz,  $C_6D_6$ )  $\delta$  128.5, 127.6, 98.3, 95.2, 92.2, 83.5 (5C), 75.8, 72.3, 72.2, 56.2, 41.8, 38.5, 35.9, 31.9 (3C), 27.6, 26.4, 22.7, 18.3, 0.52 (3C). (E)-3b:  $^{1}$ H-NMR (400MHz,  $C_{6}D_{6}$ )  $\delta$  5.80 (d, J = 16.0 Hz, 1H), 5.60 (s, 1H), 5.12 (dq, J = 16.0, 6.6 Hz, 1H), 3.55 (s, 4H), 2.43 (s, 2H), 2.11 (s, 2H), 2.29 (d, J = 6.6 Hz, 3H), 1.43 (s, 6H), 1.12 (s, 9H), 0.15 (s, 9H). (Z)-3b:  ${}^{1}$ H-NMR (400MHz,  $C_6D_6$ )  $\delta$  5.61 (s, 1H), 5.12 (dq, J = 11.0, 6.9 Hz, 1H), 4.62 (d, J = 11.0 Hz, 1H), 3.57 (s, 4H), 2.43 (s, 2H), 2.29 (d, J = 6.9 Hz, 3H), 2.11 (s, 2H), 1.43 (s, 6H),1.12 (s, 9H), 0.14 (s, 9H).
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