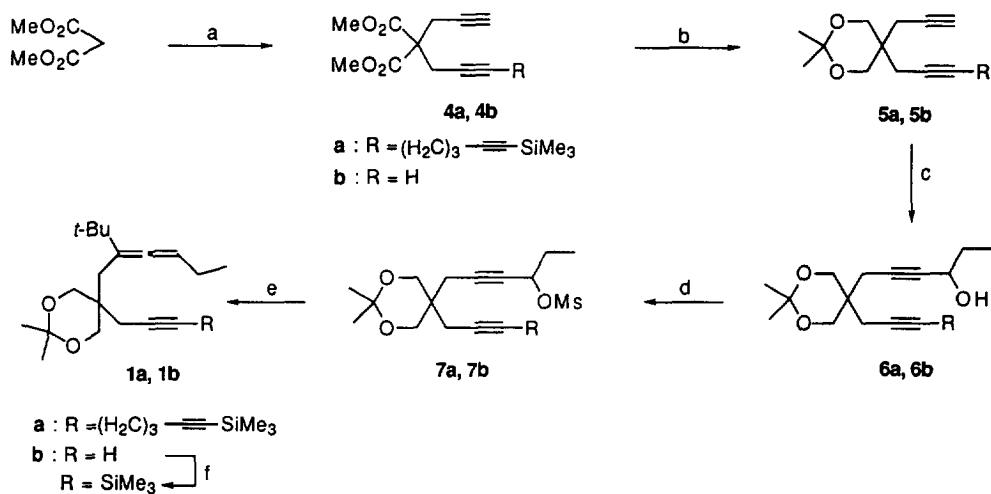




The allenynes **1** were readily prepared following scheme 2. Double alkylation of the sodium derivative of dimethylmalonate with propargyl bromide and then 1-methanesulfonyloxy-9-trimethylsilylnon-2,8-diyne or propargyl bromide provided the compounds **4a** and **4b** respectively. Reduction of the 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<sup>12</sup> from the corresponding mesylates **7** afforded the allenynes **1a** and after subsequent silylation **1b**.



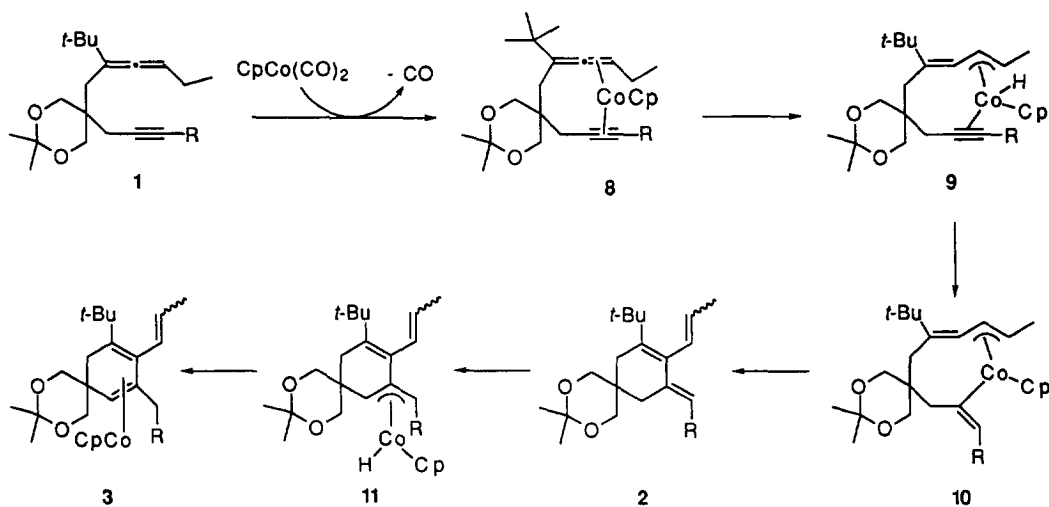
(a) **4a** : (i) NaH, BrCH<sub>2</sub>C≡CH, THF, r. t., 50% (ii) NaH, MsOCH<sub>2</sub>C≡C(CH<sub>2</sub>)<sub>3</sub>C≡CSiMe<sub>3</sub>, 73% ; **4b** : NaH, BrCH<sub>2</sub>C≡CH (2 eq.), THF, Δ, 98%. (b) (i) LiAlH<sub>4</sub>, Et<sub>2</sub>O, r. t., 1h (ii) cat. PTSA, acetone, **5a** : 73% ; **5b** : 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, ClSiMe<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)<sub>2</sub>] 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 *Z* isomers. No traces of [2+2+2] cycloadducts were observed meaning that the silylated triple bond has not reacted in the overall process. Similarly, exposure of the allenyne **1b** to CpCo(CO)<sub>2</sub> in the same conditions led to **2b** and **3b** in 60 % yield.<sup>13</sup> 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>



Scheme 3

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)<sub>2</sub> (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** : <sup>1</sup>H-NMR (400MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  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); <sup>13</sup>C-NMR (50 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  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<sub>6</sub>D<sub>6</sub>)  $\delta$  6.68 (d, *J* = 11.0 Hz, 1H), 5.49 (dt, *J* = 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<sub>6</sub>D<sub>6</sub>)  $\delta$  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** : <sup>1</sup>H-NMR (400MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  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** : <sup>1</sup>H-NMR (400MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  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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