

## Preliminary communication

 $\mu$ -[3-4- $\eta$ -(1-Alken-3-yne)]hexacarbonyldicobalt complexes:  
radical cyclocondensation mediated by manganese(III)  
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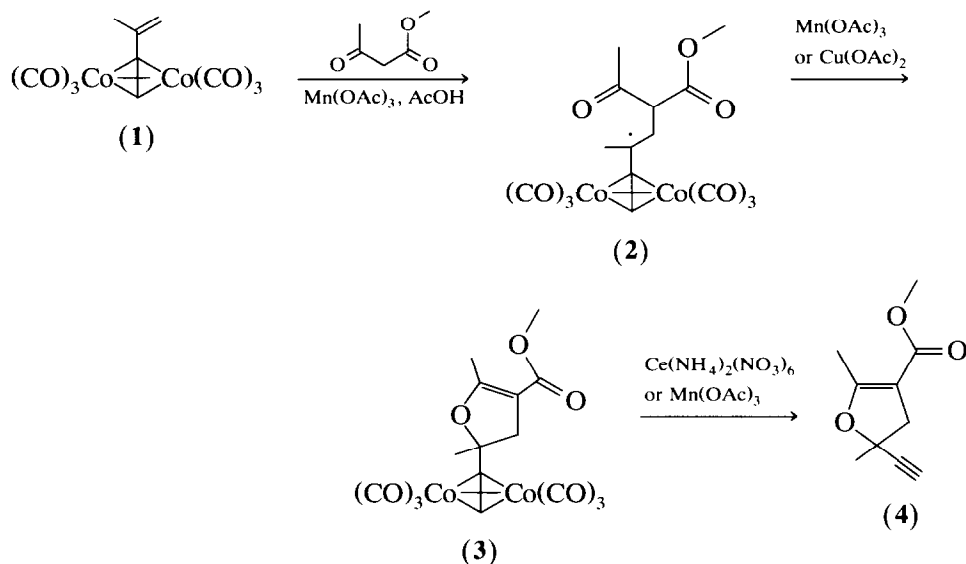
**Abstract**

A regioselective pathway for the radical reaction of 1-alken-3-yne with  $\beta$ -dicarbonyl compounds, mediated by  $\text{Mn}(\text{OAc})_3$ , can be achieved by protection of the substrate triple bond with a hexacarbonyldicobalt moiety. Dihydrofuran and hexahydrobenzofuran derivatives are formed by intermolecular oxidative cyclization of intermediate cobalt-complexed propargyl radicals.

The radical reaction of 1-alken-3-yne with  $\beta$ -dicarbonyl compounds, mediated by manganese(III) acetate, has been widely investigated in the past decade [1]. Its regiochemistry is dependent both on the type and degree of substitution of the 1-alken-3-yne, and usually double as well as triple bonds are involved [1]. We report here the regioselective version of the parent reaction which is achieved by protecting the triple bond of the 1-alken-3-yne with a hexacarbonyldicobalt (HCDC) moiety. The latter is known to be eliminated under mild conditions ( $-78$  to  $+20^\circ\text{C}$ ) by a variety of oxidating agents such as ferric nitrate [2], ceric ammonium nitrate [3,4], trimethylamine N-oxide [5], and N-methylmorpholine N-oxide [6]. Thus, the main difficulty in bringing about the  $\text{Mn}^{\text{III}}$ -mediated reaction ( $23$  to  $115^\circ\text{C}$ ) is that conditions must be found in which the rate of initial process (oxidation of  $\beta$ -dicarbonyl compounds by manganese(III) acetate [1,7]) predominates to a satisfactory extent over that of the undesired deprotection of triple bond by the same oxidant.

A standard procedure was devised for the reaction between acetoacetic acid methyl ester and  $\mu$ -[3-4- $\eta$ -(2-methyl-1-buten-3-yne)]hexacarbonyldicobalt complex (**1**). The latter was obtained by treating 2-methyl-1-buten-3-yne [8] with octacar-

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Scheme 1

bonyldicobalt as previously described [9]. By variation of the substrate/ $\text{Mn}(\text{OAc})_3$  molar ratio (1:1, 1:2, 1:4, 1:8) and the reaction temperature (20, 30, 45 °C), the best conditions were found as follows: a substrate/ $\text{Mn}(\text{OAc})_3$  molar ratio of 1:4, at 30 °C, and a reaction time of 30 min. In all cases, the amount of acetoacetic acid methyl ester was in a two-fold molar excess over  $\text{Mn}(\text{OAc})_3$ . Acetic acid was used as a solvent in an amount such that during all the experiments the concentration of  $\text{Mn}(\text{OAc})_3$  was maintained at 0.3 mol/l. Under these conditions the unwanted deprotection of the triple bond was found to range between 6–14% only.

The initiation step of the reaction is a one-electron oxidation of the acetoacetic acid methyl ester with  $\text{Mn}(\text{OAc})_3$  followed by an attack of the double bond of the HCDC-complex **1** by  $\alpha$ -acetyl- $\alpha$ -carbomethoxymethyl radical generated [10]. The intermediate cobalt-complexed propargyl radical **2** then interacts with  $\text{Mn}(\text{OAc})_3$  to form the HCDC-complex **3** via intermolecular oxidative cyclization. Subsequent decomplexation of **3** with ceric ammonium nitrate [3] yields in 4-carbomethoxy-2-ethynyl-2,5-dimethyl-2,3-dihydrofuran (**4**).

We also varied the amount of  $\text{Cu}(\text{OAc})_2$ , since the latter has been reported to play a significant role in product distribution in analogous reactions of alkenes [1,7]. But, as shown in Table 1, neither an equimolar (entry 1), nor a catalytic (entry 2) amount of  $\text{Cu}(\text{OAc})_2$  affected the reaction course or yield (entry 3). In principal, an *in situ* decomplexation of the HCDC-complex **3** can be achieved by adding the six-fold excess of manganese(III) acetate at the end of the radical reaction and subsequent heating at 45 °C for 6 h, as represented by entry 4 (Table 1), but in such a one-pot procedure the yield of product **4** is comparatively low.

The scope of the reaction was extended by using acetylacetone and 1,3-cyclohexanedione as carbonyl components and the HCDC-complexes of 1-buten-3-yne **5** [8,11] and 1-dodecen-3-yne **6** [8] as unsaturated substrates. The results of these transformations which were carried out under the conditions described

Table 1

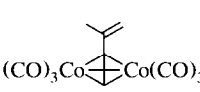
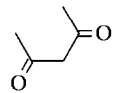
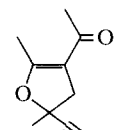
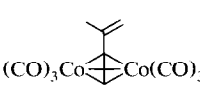
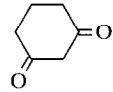
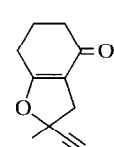
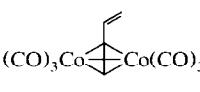
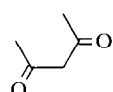
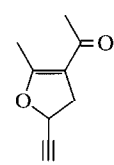
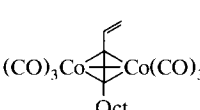
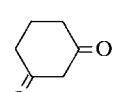
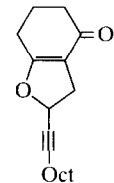
Alternative procedures for the reaction of HCDC-complex **1** with acetoacetic acid methyl ester

Entry	Molar ratio				Yield (%)	
	HCDC-complex	Acetoacetic-acid methyl ester	Mn(OAc) <sub>3</sub>	Cu(OAc) <sub>2</sub>	<b>3</b>	<b>4</b> <sup>a</sup>
1	1	8	4	1	64.5	39.0
2	1	8	4	0.05	62.1	39.5
3	1	8	4	–	65.4	40.7
4	1	8	4	0.05	<sup>b</sup>	19.1

<sup>a</sup> Overall yield. <sup>b</sup> Decomplexation of **3** *in situ* without isolation.

Table 2

Radical cyclocondensation reactions of HCDC-complexes **1**, **5**, **6** with  $\beta$ -dicarbonyl compounds, mediated by Mn(OAc)<sub>3</sub>

Starting complex	$\beta$ -Dicarbonyl compound	Product <sup>a</sup>
 <b>(1)</b>		 <b>(7)</b>
 <b>(1)</b>		 <b>(8)</b>
 <b>(5)</b>		 <b>(9)</b>
 <b>(6)</b>		 <b>(10)</b>

<sup>a</sup> After the decomplexation step.

above, are summarized in Table 2, and demonstrate the applicability of the new procedure for the synthesis of 2,3-dihydrofuran and 2,3,4,5,6,7-hexahydrobenzofuran derivatives of structures **7–10**.

Cyclocondensation products **4**, **7–10**, as well as their precursors, HCDC-complexes of type **3**, were purified by column chromatography on silica. Their satisfactory homogeneity was confirmed by GC (97–99.6% purity for decomplexation products) and TLC (single spots for HCDC-complexes). The determination of structures was based on NMR  $^1\text{H}$  (400 MHz), NMR  $^{13}\text{C}$ , MS and IR spectral data. Homo- and hetero-nuclear COSY experiments as well as NMR  $^{13}\text{C}$  spectra simulation were used to assign hydrogen and carbon atoms in the compounds synthesized.

We are currently investigating Mn<sup>III</sup>-mediated reactions of HCDC-complexes of 1-alken-3-yne, both, acyclic and cyclic, with a large variety of  $\beta$ -dicarbonyl- and related compounds.

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## References

- 1 Sh.O. Badanyan, G.G. Melikyan and D.A. Mkrtychyan, *Usp. Khim.*, 58 (1989) 475; *Chem. Abstr.* 111(1): 6532g.
- 2 K.M. Nicholas and R. Pettit, *Tetrahedron Lett.*, (1971) 3475.
- 3 D. Seyferth, M.O. Nestle and A.T. Wehman, *J. Am. Chem. Soc.*, 97 (1975) 7417.
- 4 M. Saha, S. Muchmore, D. van der Helm and K.M. Nicholas, *J. Org. Chem.*, 51 (1986) 1960.
- 5 Y. Shvo and E. Nazum, *J. Chem. Soc., Chem. Commun.*, (1974) 336.
- 6 P. Magnus and D.P. Becker, *J. Chem. Soc., Chem. Commun.*, (1985) 640.
- 7 W.J. de Klein, in W.J. Mijs and C.R.H.I. de Jonge (Eds.), *Organic Synthesis by Oxidation with Metal Compounds*, Plenum Press, New York, 1986, p. 261.
- 8 L. Brandsma, *Preparative Acetylenic Chemistry*, Elsevier, Amsterdam, 1988.
- 9 H. Greenfield, H.W. Sternberg, R.A. Friedel, J.H. Wotiz, R. Markby and I. Wender, *J. Am. Chem. Soc.*, 78 (1956) 120.
- 10 E.I. Heiba and R.M. Dessau, *J. Org. Chem.*, 39 (1974) 3456.
- 11 K.M. Nicholas and R. Pettit, *J. Organomet. Chem.*, 44 (1972) C21.