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μ-[3-4-η-(1-Alken-3-yne)]hexacarbonyldicobalt complexes: radical cyclocondensation mediated by manganese(III) acetate

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Abstract

A regioselective pathway for the radical reaction of 1-alken-3-ynes with β-dicarbonyl compounds, mediated by $Mn(OAc)_3$, 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-ynes with β-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-ynes, 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-ynes with a hexacarbonyldicobalt (HCDC) moiety. The latter is known to be eliminated under mild conditions (-78 to $+20\,^{\circ}C$) 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 Mn^{III}-mediated reaction (23 to $115\,^{\circ}C$) is that conditions must be found in which the rate of initial process (oxidation of β-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 μ-[3-4-η-(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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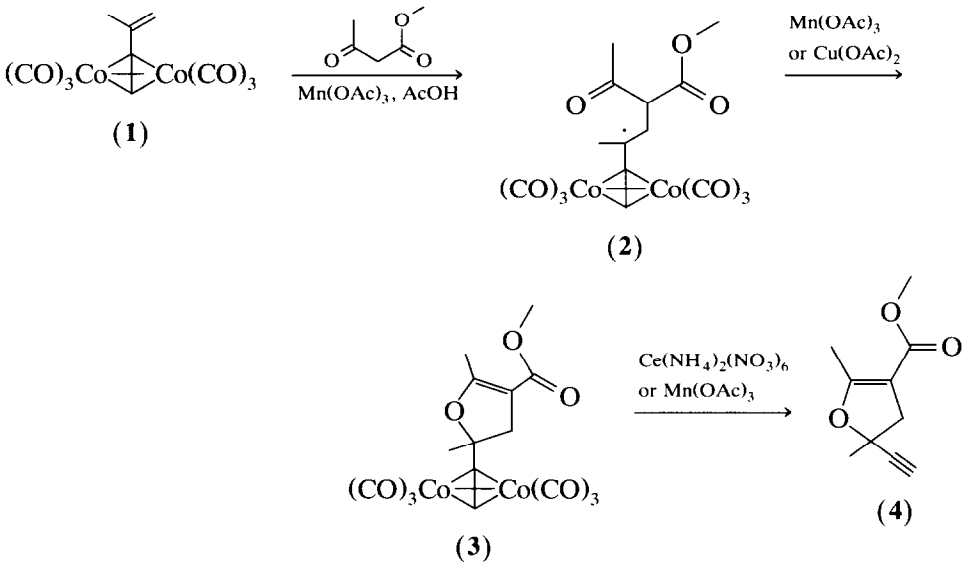


Scheme 1

bonyldicobalt as previously described [9]. By variation of the substrate/$Mn(OAc)_3$ 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/$Mn(OAc)_3$ 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 $Mn(OAc)_3$. Acetic acid was used as a solvent in an amount such that during all the experiments the concentration of $Mn(OAc)_3$ 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 $Mn(OAc)_3$ followed by an attack of the double bond of the HCDC-complex **1** by α-acetyl-α-carbomethoxymethyl radical generated [10]. The intermediate cobalt-complexed propargyl radical **2** then interacts with $Mn(OAc)_3$ 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 $Cu(OAc)_2$, 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 $Cu(OAc)_2$ 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

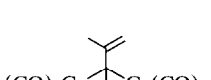
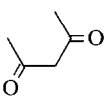
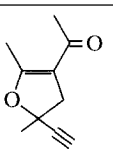
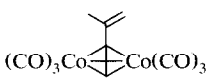
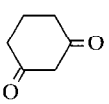
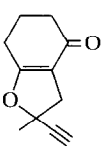
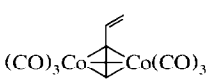
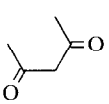
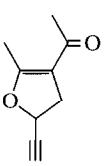
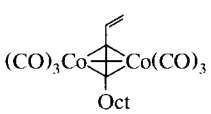
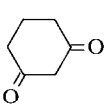
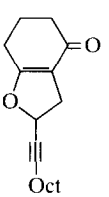
Alternative procedures for the reaction of HCDC-complex **1** with acetoacetic acid methyl ester

Entry	Molar ratio				Yield (%)	
	HCDC-complex	Acetoacetic-acid methyl ester	$Mn(OAc)_3$	$Cu(OAc)_2$	**3**	**4** [a]
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	[b]	19.1

[a] Overall yield. [b] Decomplexation of **3** *in situ* without isolation.

Table 2

Radical cyclocondensation reactions of HCDC-complexes **1**, **5**, **6** with β-dicarbonyl compounds, mediated by $Mn(OAc)_3$

Starting complex	β-Dicarbonyl compound	Product [a]
 **(1)**		 **(7)**
 **(1)**		 **(8)**
 **(5)**		 **(9)**
 **(6)**		 **(10)**

[a] 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}H (400 MHz), NMR ^{13}C, MS and IR spectral data. Homo- and hetero-nuclear COSY experiments as well as NMR ^{13}C spectra simulation were used to assign hydrogen and carbon atoms in the compounds synthesized.

We are currently investigating Mn^{III}-mediated reactions of HCDC-complexes of 1-alken-3-ynes, both, acyclic and cyclic, with a large variety of β-dicarbonyl- and related compounds.

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