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Mn(III)-mediated in-cell electrochemical addition of active methylene compounds to olefins: synthetic and mechanistic aspects

Jean-Yves Nédélec[1]*, Isabelle Lachaise[1], Khaddouj Nohair[2],
Jean Paul Paugam[1], Marjouba Hakiki[2]

[1] *Laboratoire d'électrochimie, catalyse et synthèse organique, CNRS, UMR 28*
2, rue Henri-Dunant, 94320 Thiais, France
[2] *Laboratoire des substances naturelles et de flash thermolyse,*
Faculté des sciences, Rabat, Morocco

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Summary – The Mn-mediated in-cell electrochemical addition of active methylene compounds is an interesting alternative to usual chemical methods notably with respect to the amount of manganese salt used. The electrochemical approach however requires the reagent to be readily oxidized in order to be associated with an efficient *in situ* anodic regeneration process. We have used amperometric measurements to show that the rate constants for the Mn(III)-oxidation of active methylene compounds at 60°C range between 10^{-2} and 1.2 L mol^{-1} s^{-1}. In this study we show that the addition reaction occurs in the coordination sphere of Mn; this requires the active methylene compound and the olefin to be coordinated to the Mn salt. This aspect can be critical in the electrochemical process insofar as the catalytic manganese salt can sometimes be fully coordinated by only one reagent, either the active methylene compound (*eg*, 2,4-pentanedione) or the olefin (*eg*, styrene).

electrochemistry / manganese(III) / addition reaction / free radical

Introduction

The increasing use of manganese-III as a reagent in free-radical synthetic processes [1] has stimulated the search for efficient *in situ* electrochemical generation of Mn(III) from Mn(II) in order to avoid the use of large amounts of Mn(III) [2-6]. $Mn(OAc)_2$ can indeed be easily anodically oxidized in AcOH containing AcONa or AcOK at *ca* 1 V *vs* SCE, *ie* in the presence of most organic compounds, which, apart from a few easily oxidized species, such as phenol or aniline, are themselves anodically oxidized at higher potential. However, Mn(III)-oxidation of many organic compounds is too slow to be associated with a constant *in situ* electrochemical regeneration of the oxidative manganese species at a reasonable rate. Thus the first reported electrochemical reactions involving Mn(III) were ex-cell processes [2]. The in-cell method has only recently been reported to be convenient for the addition of active methylene compounds to olefins [3,6] or the coupling reaction between acetic acid and butadiene to give sorbic acid [4].

In connection with our search for new synthetic applications of Mn(III)-promoted electrochemical C-C bond formation [5], in this paper we report a study devoted to the addition of active methylene compounds to alkenes. Some of these reactions have already been studied by Nishiguchi's group in a divided cell [3]. Our purpose was to determine to what extent an undivided cell can be used for these reactions since some limitations can be expected because side reactions can occur at the cathode (*eg*, back reduction of Mn(III)). We will compare the two methods with regard to their efficiency. We will also examine the kinetics of the Mn(III)-oxidation of compounds usually involved in such reactions, in order to select reagents which can be efficiently associated with an *in-situ* electrochemical regeneration process. Addition reactions involving Mn(III) are usually described as radical reactions [1], but the question of the very nature of the intermediate, free or complexed radicals, is still debated. We will also try to elucidate the mechanism of the reactions studied here.

Results and discussion

When we started investigating the possible addition of active methylene compounds to olefins in an undivided cell we rapidly found that, although the same adducts

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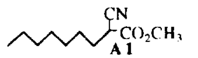
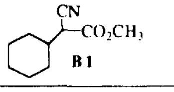
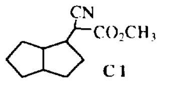
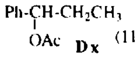
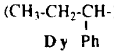
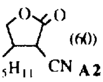
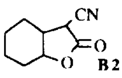
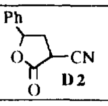
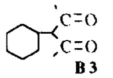
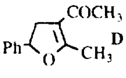
* Correspondence and reprints

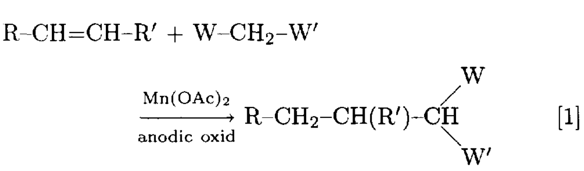
Table I. Mn-promoted electrochemical addition of either methyl cyanoacetate **1**, cyanoacetic acid **2**, or 2,4-pentanedione **3** to either 1-heptene **A**, cyclohexene **B**, 1,5-cyclooctadiene **C**, or styrene **D**[a].

Entry	Reagent	Olefin	Results in undivided cell[b] Products (yield %)	Results in divided cell Product (yield %)
1	1	A	 **A1** (17)	**A1** (51)[c]
2	1	B	 **B1** (85)	**B1** (60)[c]
3	1	C	 **C1** (54)	**C1** (76)[c]
4	1	D	 $Ph-\underset{OAc}{CH}-CH_2CH_3$ **Dx** (11)  $(CH_3-CH_2-\underset{Ph}{CH}-)_2$ **Dy** (48)	**Dx** (5)[b] **Dy** (10)[b]
5	2	A	 (60) **A2a**  **A2b** (10)	
6	2	B	 **B2** (60)	
7	2	D	 **D2** (60)	
8	3	A	no reaction	
9	3	B	 **B3** (35)	
10	3	D	 **D3** (40)	

[a] $Mn(OAc)_2$ (2 mmol), AcOK (30 mmol), reagent (20 mmol), olefin (20 mmol), $I = 0.1$ A, 2 mol electron/mol reagent, 60°C, isolated yield. [b] This work. [c] Ref 3.

were obtained, the yields were different from those obtained in a divided cell by Nishiguchi [3]. Thus, surprisingly, the coupling of methyl cyanoacetate with cyclohexene was found to be more efficient, but the coupling with hept-1-ene was found to be less efficient in the undivided cell compared with the divided one. Under both sets of experimental conditions the reactions require a charge of 2 faradays per mole of reagent which means that we are not dealing with chain reactions even if the involvement of radical intermediates usually postulated cannot be ruled out at this stage.

In order to clarify the various aspects of these Mn(III)-mediated electrochemical syntheses, we decided to investigate the behavior of typical reagents, *ie* methyl cyanoacetate **1**, cyanoacetic acid **2** and 2,4-pentanedione **3**, in the presence of various olefins (1-heptene **A**, cyclohexene **B**, 1,5-cyclooctadiene **C**, and styrene **D**). The results reported in table I include those obtained in an undivided cell, and, for comparison, those obtained in a divided cell for some of these reactions (eq 1). The reactions performed in an undivided beaker-type cell were conducted under the following experimental conditions. A solution of $Mn(OAc)_2$ (2 mmol), the reagent (**1**, **2** or **3**) (20 mmol) and the olefin (20 mmol) in AcOH (40 mL) containing AcOK (20 mmol) was electrolyzed at 60°C under constant current intensity ($I = 0.1$ A). The cell was fitted with two concentric electrodes made of glassy carbon fiber (anode; *ca* 20 cm^2) and stainless steel (cathode; *ca* 3 cm^2). The anodic reaction is the oxidation of Mn(II) at 1 V/SCE, and the cathodic reaction is the reduction of protons to form hydrogen gas. In all cases 2 faradays per mole of reagent was necessary to complete the reaction.

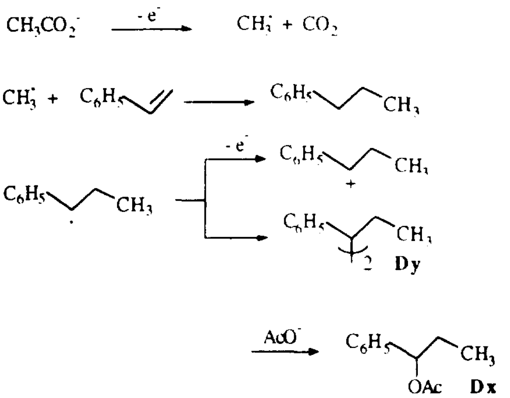


$$R-CH=CH-R' + W-CH_2-W' \xrightarrow[\text{anodic oxid}]{Mn(OAc)_2} R-CH_2-CH(R')-CH\begin{matrix} W \\ W' \end{matrix} \qquad [1]$$

W, W′ = electron-withdrawing groups

Methyl cyanoacetate **1**

The Mn-promoted addition of **1** on cyclohexene leads to high yield when performed in an undivided rather than a divided cell. In contrast, a low yield is obtained with 1-heptene in an undivided cell, whereas in a divided cell this reaction is as efficient as that performed with cyclohexene (entries 1,2, table I). Such a discrepancy prompted us to carry out the other reactions reported in table I. Good results are obtained under both experimental methods when 1,5-cyclohexadiene is used (entry 3, table I). A bicyclic adduct is selectively obtained with a *cis*-ring junction, as is usually observed in free-radical reactions involving this diene [3b]. With styrene (entry 4, table I), the adduct is not formed under either set of experimental conditions. Instead, solvent-derived products **Dx** and **Dy** were identified, which have previously been described [7] for the Kolbe reaction to generate methyl radicals (eq 2), which add to the terminal carbon of the double bond (eq 3); the benzylic radical formed can be oxidized to give **Dx** (eq 4) or dimerize into **Dy** (eq 5).



[2]

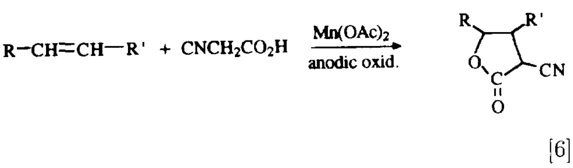
[3]

[4]

[5]

Cyanoacetic acid **2** *and 2,4-pentanedione* **3**

The main difference in the behavior between **2** and the corresponding ester **1** is the easy formation of γ-lactone adducts, instead of the saturated product (eq 6). In addition, the three types of olefins (entries 5-7, table I) gave the same type of adduct (γ-lactone) and in comparable yield (60%). This is mechanistically quite significant, as discussed below with respect to the carbohydrogenated adduct obtained with the corresponding ester.



[6]

2,4-Pentanedione **3** can be added to cyclohexene to give a saturated adduct in medium yield, while a cyclized product (**D3**, entry 10, table I) is formed with styrene, and in a slightly higher yield. However no coupling occurred with 1-heptene.

These results show that both the active methylene compound and the unsaturated compound have a key role in the reaction. In addition, there is some difference according to the method used, *ie* run in divided *vs* undivided cells. Moreover, compared with the chemical approach, which uses excess Mn(III) relative to the reagent, the results are found roughly comparable [8] as regards the nature and yield of the products. The global reaction involves many steps, and two of them could be critical, *ie* the oxidation of the reagent by Mn(III) and the regeneration of Mn(III).

Some relative rate constants are already known for the Mn(III)-oxidation of active methylene compounds [19a]. However, we have found it necessary to make a more extensive approach for this step by measuring the rate constants of Mn-oxidation of the compounds involved in our reactions. The variation of the concentration of either commercially available or electrochemically generated Mn(III) [13] in the presence of the added active methylene compound in AcOH/AcONa was monitored by recording the cathodic current at 0 V *vs* SCE at a graphite indicator electrode in an undivided electrolytic cell. It is worth noting first that Mn(III) was found to be stable for several hours at 60°C in AcOH or in aliphatic alcohols containing AcONa. In addition, all studied reagents react relatively slowly with Mn(III). Indeed, if Mn(II) is anodically oxidized in the presence of these reagents, there is no change in the cyclic voltammetric behavior on the cyclic voltammetric time scale (a few seconds at a slow 0.1 Vs^{-1} sweep rate).

General experimental conditions were first determined with the one-electron oxidation of $CNCH_2CO_2Me$ **1** as the standard reaction (eq 7), and which has been supposed to give an intermediate free radical [14]. This radical was not further oxidized by Mn(III) because it bears two electron-withdrawing groups.

$$CNCH_2CO_2Me + Mn(OAc)_3 \xrightarrow{k} CN\dot{C}HCO_2Me + Mn(OAc)_2 + AcOH \quad [7]$$

Factors other than the nature of the reagent, that may influence the rate of disappearance of Mn(III) (*eg*, nature of the solvent, temperature, nature and concentration of the supporting electrolyte, presence of an olefin) were checked separately by comparison to the following reference run. A solution of $Mn(OAc)_3$ (10^{-2} M), AcONa (5×10^{-1} M), and $CNCH_2CO_2Me$ (10^{-1} M to 6×10^{-1} M) in AcOH at 60°C was monitored electrochemically. From the data obtained at different concentrations of **1** we obtained [15] an experimental rate constant $k = 0.66 \times 10^{-2}\ M^{-1}\ s^{-1}$ for reaction [7] which is indeed relatively low. It has been checked that the disappearance of Mn(III) is due to the oxidation of methyl cyanoacetate and that, in the presence of an olefin, this leads to the formation of the adduct.

We first found that the rate constant for the above reference reaction (eq 7) increased to $2 \times 10^{-2}\ M^{-1}\ s^{-1}$ when the oxidation was carried out in the presence of 1 equiv of 1-heptene *vs* $CNCH_2CO_2Me$ and that the rate did not depend on the concentration of the olefin for a larger olefin/reagent ratio. Although the effect of the presence of the olefin was not found to be very large, we investigated the oxidation of all the other reagents in the presence of 1-heptene (10^{-1} M). We also found that the nature of the olefin itself, for example, 1-heptene, styrene or 1,5-cyclooctadiene, had no specific influence on this step. This is in keeping with Snider's report on the influence of the presence of an olefin on the Mn(III)-oxidation rate of some esters of acetoacetic acid [16].

AcOH is the usual solvent in most Mn(III)-promoted reactions. Commercial analytical-grade AcOH [17] was used as received. It has sometimes been recommended to use dry AcOH or to add Ac_2O in order to increase the overall reaction rate [18], even though negative effects of the addition of Ac_2O have also been reported [19a]. In our experiments addition of Ac_2O to the medium had no effect. However we found that a few percent of added water (> 2%) dramatically reduced the life time of Mn(III), *ie* in the presence of 5% and 10% water the concentration of Mn(III) dropped very rapidly to *ca* 85% and 30% respectively of its initial concentration. An increase of the rate of oxidation can be obtained (see table II) by using CF_3CO_2H or, more interestingly, EtOH or MeOH in the place of AcOH. EtOH was also recently reported by Snider [20] as being a convenient solvent as regards both reactivity and selectivity of some Mn(III)-promoted reactions. Mixture of solvents such as 1:1 AcOH/AcOEt can also be used, as in the work reported by Nishiguchi [3]. In all these solvents or solvent mixtures the expected product **A1** or **B1** (see table I) was formed from methyl cyanoacetate and 1-heptene or cyclohexene respectively, but we did not try to optimize these reactions for each new factor.

An acetate salt is usually used in the chemical reactions and which can supposedly [19a] act as a base to favor the enolization in reactions involving active methylene compounds. In the electrochemical reactions a supporting electrolyte is used, which is also mostly an acetate salt (AcONa, AcOK and $AcONR_4$). In both methods acetate ions have a significant influence on the reactivity of Mn(III) as indicated by the effect of the concentration of AcONa on the rate constant of the oxidation of **1** (entries 1-3, table II).

Table II. Influence of the nature of the solvent and of the concentration of the supporting electrolyte on the rate of Mn(III)-oxidation of $CNCH_2CO_2Me$[a].

Entry	Solvent	Supporting electrolyte	$10^2 \times k$ (L mol^{-1} s^{-1})
1	AcOH	AcONa (5×10^{-1})	2.0
2	"	" (7×10^{-1})	3.0
3	"	" (10×10^{-1})	4.7
4	AcOH/AcOEt (1:1)	AcONa (5×10^{-1})	2.2
	EtOH		
5	MeOH	" (5×10^{-1})	27
5	CF_3CO_2H	" (5×10^{-1})	50
7		" (5×10^{-1})	4.5

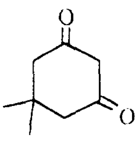
[a] $Mn(OAc)_3$ (10^{-2} M); 1-heptene (0.1 M); $CNCH_2CO_2Me$ (0.1 to 0.6 M); 60°C.

All active methylene compounds that are common reagents in Mn(III)-promoted addition reactions are oxidized at rate constants ranging between 10^{-2} and 1.2 mol $L^{-1}s^{-1}$ (table III). We can notice that acids (*eg*, **2** and **7**) are eight times as reactive as the corresponding esters (respectively **1** and **5**). As expected from a correlation with pK_a values [19] malonic acid derivatives are the slowest reagents, unless a chlorine atom is present to activate the C-H bond **6**. β-Diketones are easily oxidized, particularly in cyclic structures.

Table III. Experimental rate constants for the oxidation of various organic compounds by Mn(III) in AcOH at 60°C[a].

Entry	Organic coumpound		$10^2 \times k$ (mol $L^{-1}s^{-1}$)
1	$NC\text{-}CH_2\text{-}CO_2CH_3$	**1**	2
2	$NC\text{-}CH_2\text{-}CO_2H$	**2**	16.5
3	$CH_3COCH_2COCH_3$	**3**	4.9
4	Dimedone	**4**	120
5	$CH_2(CO_2Me)_2$	**5**	1
6	$ClCH(CO_2Et)$	**6**	67
7	$CH_2(CO_2H)_2$	**7**	8.6
8	Meldrum's acid	**8**	116

[a] $Mn(OAc)_3$ (10^{-2} M); AcONa (5×10^{-1} M); 1-heptene (10^{-1} M); organic compound (0.1 to 0.6 M).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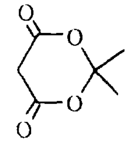
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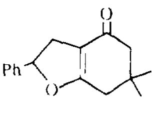
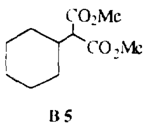
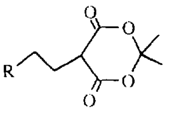
In all cases the corresponding product was obtained in preparative runs conducted according to the general method, either as indicated in table I, or as follows for the reactions not fully investigated and involving the coupling of **4** with styrene (**D4**; 65%), **5** with cyclohexene (**B5**; 25%), and **8** with 1-heptene (**A8**; 15%).



D4



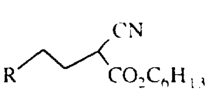
B5



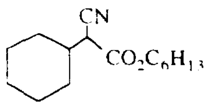
A8

Benzylic C-H-bond-containing compounds or nitromethane have also been reported [21,22] to be oxidized by Mn(III). We found that these compounds are very slowly oxidized [23] and then cannot be used in an in-cell electrochemical process. An alternative ex-cell electrochemical method can however be used, as reported by Bellamy [24] for the Mn(III)-promoted nitromethylation of aromatic compounds.

To obtain a deeper understanding of the global reaction we designed and carried out a set of experiments with hexyl cyanoacetate **9** using GC analysis to better monitor the concentration of the reagent when the coupling is not efficient. All reactions were run in an undivided cell. We first checked that in the absence of $Mn(OAc)_2$ and in the absence or the presence of an olefin the direct anodic oxidation of **9** did not occur. Moreover in the presence of $Mn(OAc)_2$ but in the absence of olefin no significant consumption of **9** was observed after passing a charge of 2 faradays per mole of **9**. In the presence of either 1-heptene or cyclohexene, **9** was consumed and with a higher rate for the cyclic olefin. The expected adducts were formed, but in yields lower than from **1** (**A9**; 7% and **B9** 15%) possibly because of steric hindrance due to the hexyl group. Apart from the unreacted starting material, hexyl cyanoacetate was found (20-30%). Thus when the addition does not occur or is rather slow, the active methylene compounds are not consumed and in an undivided cell a back reduction of Mn(III), which may be coordinated with the reagent, can occur, thus involving only Mn in the overall process.

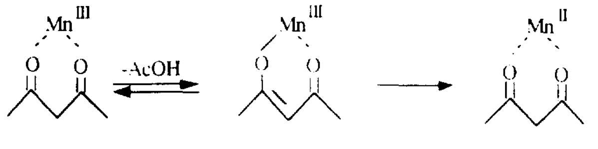


A9



B9

It is now well accepted that to be oxidized compounds have to be both acidic and enolizable in order to complex Mn(III) through a ligand-exchange process as exemplified in scheme 1 with a diketone. Indeed we can see that the fastest reaction involves a compound (dimedone, entry 4, table III) which is mainly (*ca* 95%) in the enol form [19c]. This ligand exchange is followed by an inner-sphere electron transfer [25] which would be the rate-determining step [16].



Scheme 1

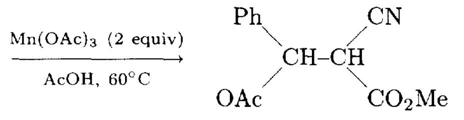
The rate constants reported in table III are probably not those for the elementary oxidation step but are more likely complex constants including pre-equilibrium, enolization, electron transfer and possibly, a reverse redox reaction (although we can neglect the concentration of Mn(II) when measuring the initial rate constant).

A simplified view of the subsequent steps would consider a diffusing free radical which can add to the C-C double bond. However, the results we have obtained can better be understood if we assume that for the reaction to be efficient the ethylenic compound must also be coordinated to the manganese, in agreement with a scheme proposed by Fristad *et al* [19b]. A mixed complexation of the two reagents with the oxidant is in keeping with the increase of the oxidation rate of the active methylene compound when an olefin is present. However, there is no correlation between the rate of Mn-oxidation of the active methylene compound and the yield in the addition reaction, since the yield of the coupling product strongly depends on the nature of the olefin. It should also be taken into account that in the electrochemical procedures only a small amount of manganese is used.

Accordingly, on the basis of the reaction occurring in the coordination sphere of Mn, we can consider three cases depending on the relative equilibrium constants between the various reagents and Mn(III). Thus, either the active methylene compound or the ethylenic compound can better coordinate Mn(III) than the other reagent. Alternatively the two reagents have equilibrium constants of the same order. This can be well illustrated with styrene. Thus, when **1** is reacted with styrene only the side reactions leading to **Dx** and **Dy** (eq 2–5) occur and during the reaction the anode potential rapidly reaches 2 V/SCE. Moreover when MeOH is used as a solvent the expected adduct is not formed and the only reaction occurring is the methoxylation of styrene. In the kinetic investigation we have found that the disappearance of Mn(III) by reaction with methyl cyanoacetate is not greatly modified by the presence of styrene. In keeping with this, we have found that the adduct **D1** can be obtained efficiently (60%) according to the usual chemical approach, *ie* in the presence of at least 2 equiv of Mn(III) relative to **1** (eq 8).

$Ph\text{-}CH{=}CH_2 + CNCH_2CO_2Me$

D **1**



$$\xrightarrow[\text{AcOH, 60°C}]{\text{Mn(OAc)}_3\text{ (2 equiv)}} Ph(OAc)CH\text{-}CH(CN)CO_2Me \quad [8]$$

D1

The limitation for this electrochemical reaction is the regeneration of Mn(III). It can be easily shown by cyclic voltammetry that the oxidation of Mn(OAc)$_2$ in AcOH and in the presence of styrene does not occur at 1 V/SCE as it does in the absence of styrene, and is probably shifted positively to the region corresponding to the oxidation of the solvent, thus indicating a strong interaction of Mn and styrene. All attempts to characterize any new complex failed. The absence of an Mn complex oxidizable at *ca* 1 V/SCE enables the oxidation of acetate ion leading to the Kolbe reaction. On the other hand, when cyanoacetic acid **2** is reacted with styrene, a good yield of the lactone **D2** is obtained (entry 7, table I). More generally, **2** appears to allow an efficient formation of a 1:1 olefin reagent complex with Mn, whatever the olefin. This enables the coupling reaction to occur easily. In addition, the intermediate radical species is likely kept in the coordination sphere, since it is further oxidized into the γ-lactone product. This is clearly indicative of a reaction occurring in the coordination sphere of Mn. Finally, 2,4-pentanedione **3** should strongly coordinate to Mn, thus preventing or restricting the complexation of the olefin, even if it is styrene since only 40% of the cyclic adduct is formed.

In conclusion, we first repeat that the Mn-promoted electrochemical addition of active methylene compounds is an interesting alternative for the usual chemical reactions using Mn(III) in high concentration. The electrochemical reactions can be run in-cell in many cases where the Mn-oxidation of the reagent is rapid enough. It also appears from this study that the addition reaction takes place in the coordination sphere of the manganese. An undivided cell can be used with the same efficiency as a divided cell. There is however a severe limitation which can result from a strong coordination of a reagent with Mn which is used in catalytic amount. This effect is a major drawback for runs in undivided cells since the complex formed can be oxidized and reduced without leading to any product. Regarding the question of a possible radical mechanism, diffusing free-radicals as key intermediates are unlikely. It should be added, however, that, as we have shown in previous studies [5], we can easily initiate typical free radical chain addition reactions of halo compounds to olefins by oxidizing electrochemically Mn(OAc)$_2$ in the presence of equimolar amount of methyl cyanoacetate or 2,4-pentanedione.

Experimental section

General

NMR spectra were recorded on a Bruker AC 200 E spectrometer in CDCl$_3$. Mass spectra were obtained on a Finnigan ITD 800 spectrometer coupled to a Varian 3 300 chromatograph with a 0.12 μ SIL-5 (25 m × 0.32 mm) silica-fused capillary column. Gas chromatography was performed on a Varian 3 300 chromatograph with a 0.5 μ SIL-5 (5 m × 0.32 mm) silica-fused capillary column. Reagents, solvents and supporting electrolytes were used as obtained commercially. The electrochemical undivided cell was cylindrical with the top fitted with five SVL necks allowing electric and gas connections as well as sampling for monitoring the reaction. The two compartments of the divided cell were separated by a glass frit. The metals used as electrodes were commercial. All reactions were carried out at 40 or 60°C in air.

Kinetic measurements

As indicated in the text the measurements can be performed with commercial as well as electrogenerated Mn(OAc)$_3$. For practical purposes the commercial salt was used. The undivided cell was fitted with a working carbon microelectrode, an auxiliary electrode made of carbon fiber, and a saturated calomel reference electrode. To a solution of AcONa in 40 ml of the selected solvent at 60°C (see table I) was added Mn(OAc)$_3$ (20 mmol). The stability of the oxidant was first checked by amperometric monitoring for a few minutes. Chronoamperometric monitoring in the presence of the organic reagents was made at 0 V/SCE.

Typical procedure for the addition of active methylene compounds

A solution of Mn(OAc)$_2$ (2 mmol), the reagent (**1**, **2**, or **3**) (20 mmol), and the olefin (20 mmol) in AcOH (40 mL) containing AcOK (20 mmol) was electrolyzed at 60°C under constant current intensity (I = 0.1 A), the cell being fitted with two concentric electrodes made of carbon fiber (anode; *ca* 20 cm^2) and stainless steel (cathode; *ca* 3 cm^2) and connected to a constant-current power supply. In all cases 2 faradays per mole of reagent were necessary to complete the reaction. After the electrolysis, AcOH was removed under vacuum, then the mixture was diluted in diethylether or CH$_2$Cl$_2$ and washed with water. Products were purified by chromatography on silica gel with pentane/diethylether.

Identification of the products

- *1-Phenylpropyl acetate* (**Dx**)

It was characterized by comparison of its GC and spectral data with those for an authentic sample prepared by acetylation of the commercial corresponding alcohol 1-phenyl propan-1-ol.

^{1}H NMR δ 7.2 (m, 5H), 5.6 (t, 1H), 2 (s, 3H), 1.8 (m, 2H), 0.9 (t, 3H).

^{13}C NMR 170, 140, 128.9, 128.2, 127.8, 126.4, 125.9, 77, 29, 21, 9.75.

GC-MS (relative intensity) 149 (10.4), 136 (38), 117 (28), 107 (58), 91 (30), 79 (20), 65 (6), 51 (18), 43 (100).

A9 and **B9** were characterized by GC comparison with **A1** and **B1**, respectively, after conversion into the corresponding methyl esters.

The following products were characterized by comparison of their spectral data with those given in the cited references:

- *Methyl 2-cyanononanoate* (**A1**) *[3]*

^{1}H NMR δ 3.75 (s, 3H), 3.46 (t, 1H), 1.92 (m, 2H), 1,1 (m, 10H), 1 (t, 3H).

^{13}C NMR 166, 116, 53, 37, 31, 29.7, 28.7, 28, 26, 22, 14.

- *2-Oxo-4-pentyl-tetrahydrofuran-3-carbonitrile [9]*

It was characterized as its methyl ester (**A^{2}a**).

^{1}H NMR δ 4.5 (OH), 3.75 (s, 3H), 3.58 (m, 1H), 2.7-2 (m, 2H), 1.2-1 (m, 9H), 0.95 (t, 3H).

^{13}C NMR 168, 116, 80, 53, 47, 35.3, 31.8, 31.3, 28.8, 24.7, 22.4, 13.

- *Methyl 2-cyano-2-cyclohexylacetate* (**B1**) *[3]*

^{1}H NMR δ 3.84 (s, 3H), 3.42 (d, 1H), 2.09 (m, 1H), 1.76 (m, 5H), 1.27 (m, 5H).

- *2-Oxo-octahydrobenzofuran-3-carbonitrile* (**B2**) *[11]*

It was characterized as its methyl ester.

^{1}H NMR δ 4.64 (OH), 3,74 (s, 3H), 3.29 (d, 1H), 2.7 (m, 1H), 1.8-1.4 (m, 9H).

^{13}C NMR δ 168, 116, 78, 53, 52.7, 39, 27.8, 26, 21.8, 20.

- *3-Cyclohexyl-2,4-pentanedione* (**B3**) *[12]*

^{1}H NMR 3.5 (d, 1H), 2.2 (s, 6H), 1.5 (m, 11H).

GC-MS (relative intensity) 183 (10), 101 (48), 82 (7), 67 (12), 59 (12), 43 (100).

- *Dimethyl cyclohexylmalonate* (**B5**) *[3]*

^{1}H NMR δ 3.66 (s, 6H), 3.46 (d, 1H), 1.8 (m, 11H).

- *Methyl 2-(exo-bicyclo [3.3.0] oct-2-yl)-2-cyanoacetate* (**C1**) *[3]*

^{1}H NMR δ 3.7 (s, 3H), 3.5 (d, 1H), 2.4-1 (m, 13H).

^{13}C NMR 166, 115, 52, 47, 43, 41, 32.8, 32.7, 32.6, 32.3, 32.2.

- *Methyl 4-acetoxy-2-cyano-4-phenylbutanoate* (**D1**)

1/1 mixture of diastereomers.

^{1}H NMR δ 7.2 (broad s, 5H), 5.8 (m, 1H), 3.7 and 3.65 (two s, 3H), 3.5 (m, 1H), 2.4 (m, 2H), 2 and 1.95 (two s, 3H).

^{13}C NMR δ 169.54 and 169.5, 165.63 and 169.60, 138.17 and 136.08, 128.5, 127.35, 126.4, 115.57 and 115.47, 72.82 and 72.28, 53.40, 3570 and 35.57, 33.94 and 33.70, 20.66.

GC-MS (relative intensity) 246 (1.8), 218 (47), 202 (100), 186 (34), 170 (28), 143 (26), 121 (40), 103 (33), 77 (16).

HRMS calc for C$_{14}$H$_{15}$NO$_4$Li: 268.2157. Found: 268.1154.

- *2-Oxo-5-phenyltetrahydrofuran-3-carbonitrile* **(D2)** *[9]*

^{1}H NMR δ 7.3 (5H), 5.4 (dd, 1H), 3.87 (dd, 1H), 3 (m, 1H), 2.5 (m, 1H).

^{13}C NMR δ 167.7, 136.8, 129.6, 129.2, 128.2, 125.7, 124.9, 114.5, 80.7, 36.1, 33.4.

GC-MS (relative intensity) 187 (50), 160 (9), 143 (86), 116 (100), 105 (91), 77 (76), 63 (27), 51 (98).

Anal calc for $C_{11}H_9NO_2$: C, 70.58; H, 4.84; N, 7.48; O, 17.09. Found: C, 70.49; H, 5.15; N, 7.39; O, 16.97.

- *4-Acetyl-5-methyl-2-phenyl-2,3-dihydrofuran* **(D3)** *[10]*

^{1}H NMR δ 7.31 (m, 5H), 5.54 (dd, 1H), 2.91 (dd, 1H), 2.27 (s, 3H), 2.14 (s, 3H).

^{13}C NMR d 190, 167, 145, 128.5, 127.5, 126.1, 126, 125.6, 117, 83, 38.5, 29, 15.

GC-MS (relative intensity) 199 (12), 154 (30), 139 (80), 113 (47), 111 (30), 98 (99), 94 (64), 81 (85), 67 (92), 55 (100).

- *6,6-Dimethyl-2-phenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one* **(D4)** *[26]*

^{1}H NMR δ 7.07 (m, 5H), 5.5 (dd, 1H), 3.05 (dd, 1H), 2.6 (dd, 1H), 2.11 (s, 2H), 2 (s, 2H), 0.85 (s, 6H).

^{13}C NMR δ 194.65,176.55, 140.6, 128.62, 128.3, 125.6, 111.15, 86.43, 50.55, 37.54, 33.95, 33.7, 28.6, 28.3.

GC-MS (relative intensity) 243 (100), 185 (33), 171 (41), 144 (28), 129 (30), 115 (81).

- *3,4-Diphenylhexane* **(Dy)** *[18]*

^{1}H NMR 7.2 (m, 10H), 2.5 (m, 2H), 1.25 (m, 4H), 0.45 (t, 6H).

^{13}C NMR 142, 128.7, 128.1, 127.9, 126.2, 125.7, 54 , 27, 12.

GC-MS (relative intensity) 119 (47), 118 (39), 91 (100), 77 (10).

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