

# Cerium (IV) ammonium nitrate as an efficient catalyst for oxidation of alkyl malonates into ketomalonates by dioxygen

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## Abstract

The synthesis of diethyl ketomalonate via direct oxidation of diethyl malonate by pure oxygen or even using air, in the presence of cerium ammonium nitrate (CAN) used in catalytic amount is reported. The efficiency of this new catalytic system toward this reaction is compared to the previously described  $\text{Co}^{\text{III}}\text{--Mn}^{\text{III}}$  catalyst. Thus, when  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  was used, oxidation occurred in acetic acid–acetonitrile medium (1/1 v/v) under oxygen flow at moderate temperature (50–70°C) and with excellent selectivity (> 90%). In contrast, the Co/Mn catalyst required higher temperature (80–120°C) and the selectivity for the desired product drastically decreased with conversion. Under the latter conditions, a great part of the reaction products and/or substrate is degraded into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Moreover, with CAN system, an appreciable yield could be obtained under air flow (or even only by stirring under air) whilst with Co/Mn, under the same conditions, the conversion was very low. Finally the separation of CAN from reaction products and solvents at the end of the reaction and its reuse could be facilitated by coating CAN on porous silica. This supported CAN/ $\text{SiO}_2$  system exhibited in its first use the same activity as free CAN and in its second use about 70% of the initial value. © 1997 Elsevier Science B.V.

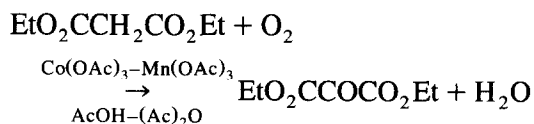
**Keywords:** Malonate oxidation; Ketomalonates; Cerium–ammonium nitrate

## 1. Introduction

Diethyl ketomalonate (DKM) is an important versatile reagent for organic synthesis. Actually, it can react in a wide selection of C–C bond forming processes including Diels–Alder [1,2], Friedel–Crafts [3,4], aldol [5] and ene [6–8] reactions.

Different syntheses of this ketoester have been previously reported, in particular from diethyl malonate (DEM). However, they often present the major drawback which is difficult to carry

out [9] and/or to need expensive co-reactant such as bromine [10,11] and to lead in this case to the formation of undesirable co-products. Therefore, direct oxidation of diethyl malonate by oxygen or air is economically and ecologically more attractive. Thus, a recent patent [12] that reports this synthesis catalysed by the mixture  $\text{Co}^{\text{(III)}}/\text{Mn}^{\text{(III)}}$  acetates has attracted our attention (Eq. (1)).



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On the other hand, the  $\text{Ce}^{\text{IV}}$  ammonium nitrate (CAN) is a well known oxidizing agent, which can be used stoichiometrically to oxidize secondary alcohols into ketones [13–15] or benzylic groups into aldehydes [16–18]. In the same way, it was reported that this compound promotes either in stoichiometric or catalytic amounts the addition of dimethyl malonate to various aromatic compounds [19]. However, to our knowledge, oxidation of malonate esters by CAN has never been reported.

Here, we wish to present the results of our investigations on the oxidation of diethyl malonate by molecular oxygen catalysed by CAN and to compare the efficiency of this system with the one of the previous Co–Mn catalyst.

## 2. Experimental

### 2.1. Materials

All reactants, solvents, and catalysts (except  $\text{Co}(\text{OAc})_3$  and  $\text{Co}(\text{acac})_3$ ) were purchased in their highest purity from Aldrich Chemical or Janssen Chemical and used without further purification.  $\text{Co}(\text{acac})_3$  was supplied by Siccanor (Douchy, France). The silica gel (70–230 mesh, pore diameter 60 Å) was purchased from Merck. Pure oxygen was used directly from a cylinder (air liquide).

#### 2.1.1. Preparation of $\text{Co}(\text{OAc})_3$

Solutions of Co(III) acetate in acetic acid were prepared electrolytically with platinum electrodes using NaOAc, at the concentration corresponding to the one used in the oxidation experiment, as the electrolyte [20,21]. The electrolysis was performed at room temperature and at ca. 10 V, in a glass divided cell in which the anodic and cathodic compartments are separated by a fritted glass disk. At the end of the electrolysis, the concentration of the Co(III) in the anodic solution was determined by iodometric titration of an aliquot, and a part of the solution containing a standard amount of Co(III) was

directly used for oxidation experiment after addition of diethyl malonate, acetic anhydride and  $\text{Mn}(\text{OAc})_3$ .

#### 2.1.2. Preparation of CAN/ $\text{SiO}_2$ catalyst

To a solution of CAN (3.5 g, 6.2 mmol) in a mixture of methanol (26 ml) and dichloromethane (17 ml) was added silica (17.5 g). After stirring for 30 mn, the solvents were removed by evaporation and the solid was dried under vacuum at 80°C until a finely divided yellow powder was obtained (4 h).

### 2.2. Apparatus

Gas chromatography analyses were carried out on a Delsi 300 or a Chrompack 9001 gas chromatograph equipped with a fused silica capillary column: CP Sil 5-CB (25 m  $\times$  0.32 mm, Chrompack) for general separation. GC–MS coupled analyses were performed with a concept II spectrometer (Kratos Analytical) using a DB1 capillary column (25 m  $\times$  0.25 mm).

### 2.3. General procedure for diethyl malonate oxidation

#### 2.3.1. Catalysed by $\text{Co}^{\text{III}}\text{–Mn}^{\text{III}}$

In a typical experiment, a 50 ml round-bottom flask equipped with a reflux condenser, a magnetic stirrer and an oxygen inlet, was charged with a solution of diethyl malonate (62.4 mmol, 10 g) in acetic acid (15 ml) and acetic anhydride (6.5 ml). The catalyst and sodium acetate (if specified) were added to the mixture. Oxygen was then gently bubbled through the solution and its flow adjusted according to the indication of a flow meter. The mixture was heated by means of an oil bath to the desired temperature under stirring. 1 ml aliquots were withdrawn from the reaction mixture at various times, their exact mass was determined and a precise amount of dimethyl malonate as internal standard for GC analyses was added. Then the mixture was extracted several times with diethyl ether after addition of

water. The organic phase was dried over  $\text{Na}_2\text{SO}_4$  and analysed by capillary GC for conversion, selectivity and yield determination. According to the reproducibility of the chromatographic results the overall error between the different experiments can be estimated to about 1% for conversion and 2% for selectivity which is determined by difference.

### 2.3.2. Catalysed by CAN

The same procedure was used except that the solvent and the amount of dimethyl malonate were different and are specified in the tables.

## 3. Results and discussion

### 3.1. Oxidation of diethyl malonate catalysed by the $\text{Co}^{\text{III}}\text{--Mn}^{\text{III}}$ system

In order to make direct comparisons of the CAN based catalyst system with the previous Co–Mn system, we have studied the behavior of the latter under standard conditions.

Thus, when a solution of diethyl malonate in a mixture of acetic acid and acetic anhydride was heated at  $130^\circ\text{C}$  in the presence of a catalytic amount of  $\text{Co}(\text{OAc})_3\text{--Mn}(\text{OAc})_3$  and

stirred under a pure oxygen flow, a 21% yield of diethyl ketomalonate was obtained after 4 h (Table 1, entry 1). The substitution of  $\text{Co}(\text{OAc})_3$  by  $\text{Co}(\text{acac})_3$  (acac = acetyl acetonate), a commercially available product unlike  $\text{Co}(\text{OAc})_3$  which has to be synthesized before use, led to a surprising increase in activity, yielding 52% of DKM (Table 1, entry 2). On the other hand, the replacement of  $\text{Mn}(\text{OAc})_3$  by  $\text{Mn}(\text{acac})_3$  with  $\text{Co}(\text{acac})_3$  as the cocatalyst, had a weak effect on the efficiency of the reaction although the selectivity into DKM increased (Table 1, entries 7 and 9). Actually, although no other species than DKM could be detected by chromatographic analyses in the reaction medium at the end of the reaction, the mass balance indicated that the amount of DKM formed was often very much lower than that of diethyl malonate which had reacted. From various experiments conducted at different temperatures and catalyst concentrations, we deduced that the loss of DKM increased and consequently the selectivity drastically decreased with the conversion (see Table 1, entries 2, 5–8). Under these conditions an important part of the substrate and/or of the reaction products was degraded into  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{HCOOH}$  and ethyl acetate. These last compounds were detected by GC/MS coupling

Table 1  
Oxidation of diethyl malonate catalysed by the system  $\text{Co}^{\text{III}}\text{--Mn}^{\text{III}}$  a

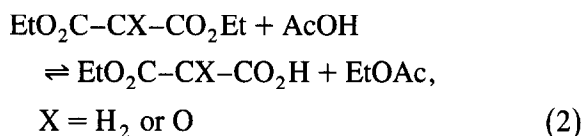
No.	Catalytic system (mmol)	Time (h)	Temperature ( $^\circ\text{C}$ )	Conv. <sup>b</sup> (%)	Selectivity into DKM <sup>c</sup> (%)	Yield (%)
1	$\text{Co}(\text{OAc})_3$ (1.1) $\text{Mn}(\text{OAc})_3$ (1.1)	4	130			21
2	$\text{Co}(\text{acac})_3$ (1.1) $\text{Mn}(\text{OAc})_3$ (1.1)	4	130	99	53	52
3	$\text{Co}(\text{acac})_3$ (2.2)	5	80	17	97	16
4	$\text{Mn}(\text{OAc})_3$ (2.2)	5	80	41	96	39
5	$\text{Co}(\text{acac})_3$ (0.28) $\text{Mn}(\text{OAc})_3$ (0.28)	5	80	43	96	41
6	$\text{Co}(\text{acac})_3$ (0.56) $\text{Mn}(\text{OAc})_3$ (0.56)	5	80	50	76	38
7	$\text{Co}(\text{acac})_3$ (1.1) $\text{Mn}(\text{OAc})_3$ (1.1)	5	80	70	60	42
8	$\text{Co}(\text{acac})_3$ (2.2) $\text{Mn}(\text{OAc})_3$ (2.2)	5	80	87	55	57
9	$\text{Co}(\text{acac})_3$ (1.1) $\text{Mn}(\text{acac})_3$ (1.1)	5	80	56	90	50
10	$\text{Co}(\text{acac})_3$ (1.1) $\text{Mn}(\text{acac})_3$ (1.1)	5	80	53	92	48
11	$\text{Co}(\text{acac})_3$ (1.1) $\text{Mn}(\text{acac})_3$ (1.1)	5	80	80	49	39
12	$\text{Co}(\text{acac})_3$ (1.1) $\text{Mn}(\text{acac})_3$ (1.1)	8	130	25	1	2

<sup>a</sup> Conditions: diethyl malonate = 62.4 mmol; acetic acid = 15 ml; acetic anhydride = 6.5 ml;  $\text{NaOAc}$  = 18 mmol except entries 10 and 11: 36 and 0 mmol respectively; oxygen flow rate = 5 l/h except entry 12 air flow rate = 15 l/h.

<sup>b</sup> DEM conversion, determined by GC analysis, using dimethyl malonate as internal standard.

<sup>c</sup> Defined as the number of moles of DKM formed per number of moles of consumed DEM.

analyses after trapping the off gas at liquid nitrogen temperature. EtOAc probably arises from a transesterification reaction between DEM or/and DKM and the solvent (AcOH) according to the following reaction (Eq. (2)).



The fact that the ketoacid **1** (X = O) obtained from this process is much more susceptible to undergo decarboxylation catalysed by  $\text{Mn}(\text{OAc})_3$  than the corresponding ester [22], probably accounts for the lack of selectivity observed at high conversion and high temperature.

It is also noteworthy that in the above mentioned patent [12], the use of an alkaline salt of a carboxylic acid is claimed, so that, we have examined the effect of NaOAc on the reaction. It appeared that the activity decreased and the selectivity increased with increasing concentration of NaOAc (Table 1, entries 9–11). Consequently the yield passed through a maximum for a NaOAc/catalyst ratio of about 8.

Finally, when air was used instead of pure oxygen, the activity drastically decreased, even at comparable net oxygen flowrate. Indeed at 80°C, the conversion tended toward zero. At higher temperature, the conversion slightly increased but the selectivity into DKM was very low (Table 1, entry 12).

In conclusion, the Co–Mn based system catalyses the oxidation of diethyl malonate into diethyl ketomalonate by dioxygen. However, the selectivity of the reaction drastically decreases as the conversion increases, as an important part of the reaction products and/or substrate is degraded via further oxidation under these conditions. Furthermore, when air is used as oxygen source, the yield is very poor.

### 3.2. Oxidation of diethyl malonate catalysed by CAN

#### 3.2.1. Solvent effect

Stoichiometric oxidations of organic compounds by CAN are achieved in various solvents including water [23], methanol [18], acetic acid [23], acetonitrile [13,15]. It was therefore of interest to compare the activity of CAN vs. DEM catalytic oxidation in different solvents.

In water or alcohols, in which CAN is still widely soluble, the reaction was totally inhibited (Table 2, entries 1–3). In pure acetonitrile or acetic acid, moderate yields but excellent selectivities were observed although CAN is only weakly soluble in AcOH. The use of a AcOH–MeCN mixture (1/1, *v/v*) as solvent, allowed to conjugate the beneficial effect of each component and led to a 74% conversion after 5 h reaction time at only 50°C, with a nearly total selectivity throughout the whole reaction time (see Table 2, entry 7). The addi-

Table 2  
Oxidation of diethyl malonate into diethyl ketomalonate catalysed by CAN<sup>a</sup>

No.	Solvent ( <i>v/v</i> )	Temperature (°C)	<i>t</i> (h)	Conv. (%)	Selectivity (%)	Yield (%)
1	MeOH	50	5	0	—	—
2	AcOH/H <sub>2</sub> O (3/1)	50	5	0	—	—
3	EtOH	50	5	0	—	—
4	AcOH/EtOH (1/1)	50	5	7	100	7
5	AcOH	50	5	23	100	23
6	MeCN	50	5	17	100	17
7	AcOH/MeCN (1/1)	50	5	74	100	74
8	AcOH/(Ac) <sub>2</sub> O/MeCN(1/1/1)	50	5	75	86	65
9	AcOH–MeCN (1/1)	70	3	82	94	77
10	AcOH–MeCN (1/1)	90	3	75	90	68

<sup>a</sup> Conditions: diethyl malonate = 32 mmol; CAN = 3.1 mmol; solvent(s) 20 ml total volume; O<sub>2</sub> = 5 l/h.

tion of acetic anhydride, used to maintain anhydrous conditions as in the case of the Co–Mn catalyst, was not necessary and had rather a detrimental effect on the selectivity (Table 2, entry 8).

### 3.2.2. Effect of the temperature

The temperature effect was investigated in the 50 to 90°C range (Table 3). When CAN was used as the catalyst, at a temperature as low as 50°C, an appreciable yield of DKM was obtained (74%). When the temperature increased from 50° to 70°C, a weak improvement of the conversion was observed but the selectivity decreased (compare Table 3, entries 1–2). Up to 70°C, a further increase of the temperature resulted in the decrease of both conversion and selectivity, and at 90°C the yield was lower than the one obtained at 50°C.

### 3.2.3. Effect of the nature of gas and related flow rates

Preliminary experiments were conducted with pure oxygen with a flowrate of 5 l/h, i.e. largely superior to the stoichiometric demand. Decreasing twofold this flow had a slight effect on the yield of the reaction. Interestingly, when pure oxygen was replaced by air, ca. 60% conversion was achieved in 3 h. Although this result was lower than that obtained with pure oxygen, the reaction was much less inhibited in the presence of air than with the Co–Mn catalyst. Moreover an air flow was not imperatively

needed, as yields of 16% and 60% were observed after 3 h and 48 h respectively, when the reaction medium was only stirred under air.

### 3.2.4. Effect of the amount of catalyst and promoter

Table 4 shows the influence of the catalyst concentration on the conversion and the selectivity of the reaction (entries 1–4). While a ratio CAN vs. substrate of 0.1 afforded, at 70°C, a conversion of 82%, decreasing this ratio to 0.05 drastically dropped the conversion to 17% (entry 2). On the other hand, doubling the initial ratio had only a limited effect on the conversion that increased from 82% to 92%.

Assuming a radical process and owing to the known ability to Co(II) salts to cleave potential peroxides (see for example Ref. [24]), Co(OAc)<sub>2</sub> was added to the reaction medium as a promoter. From a series of experiments carried out under these conditions, one can deduce the following statements:

(i) At 50°C, the presence of Co(OAc)<sub>2</sub> improved the yield of DKM from 74% to 90% even at low concentration of Co(OAc)<sub>2</sub> vs. CAN (Table 4, entry 5).

(ii) At 70°C, for a CAN/substrate ratio = 0.1, Co(OAc)<sub>2</sub> had rather a harmful effect, that increased with the cobalt content (Table 4, entries 6 and 7).

(iii) At the same temperature but for a lower CAN concentration (CAN/substrate = 0.05), the effect of addition of Co(OAc)<sub>2</sub> was opposite

Table 3  
Influence of physical parameters on the oxidation of diethyl malonate catalysed by CAN<sup>a</sup>

No.	Temperature (°C)	Nature of gas	Flow rate (l/h)	t (h)	Conv. (%)	Selectivity (%)	Yield (%)
1	50	O <sub>2</sub>	5	5	74	100	74
2	70	O <sub>2</sub>	5	5	84	94	79
3	90	O <sub>2</sub>	5	5	77	90	69
4	70	O <sub>2</sub>	5	3	82	94	77
5	70	air	8	3	60	85	51
6	70	air	5	3	57	88	50
7	70	air	0	3	16	100	16
8	70	air	0	48	60	100	60
9	70	N <sub>2</sub>	0	10	20	90	18

<sup>a</sup> Conditions: diethyl malonate = 32 mmol; CAN = 3.12 mmol; acetic acid = 10 ml; acetonitrile = 10 ml.

Table 4

Oxidation of diethyl malonate into diethyl ketomalonate; influence of CAN amount and cocatalyst <sup>a</sup>

No.	CAN (mmol)	Cocatalyst (mmol)	Temp. (°C)	Conv. (%)	Selectivity (%)	Yield (%)
1	1.5	–	70	17	100	17
2	3.12	–	70	84	94	79
3	6.24	–	70	92	100	92
4	3.12	–	50	74	100	74
5	3.12	Co(OAc) <sub>2</sub> (0.52)	50	90	100	90
6	3.12	Co(OAc) <sub>2</sub> (0.52)	70	80	98	78
7	3.12	Co(OAc) <sub>2</sub> (1.04)	70	74	98	72
8	1.5	Co(OAc) <sub>2</sub> (0.52)	70	42	94	39

<sup>a</sup> Conditions: diethyl malonate = 32 mmol; acetic acid = 10 ml; acetonitrile = 10 ml; 5 h; O<sub>2</sub> = 5 l/h.

to that mentioned above as 39% yield was obtained with Co instead of 17% (Table 4, entry 8).

From these features, one can assume that the rate determining step of the catalytic cycle is probably different at 50°C and 70°C.

### 3.3. Oxidation of diethyl malonate catalysed by CAN supported on silica

In order to facilitate the isolation and the recycle of the catalyst from the products and solvents at the end of the reaction, CAN was supported on porous silica [25]. The CAN/SiO<sub>2</sub> reagent (cerium ammonium nitrate coated on silica) was obtained as a free-flowing yellow powder at the concentration of 0.22 g of CAN per gram of silica and used at the same Ce/substrate ratio as in the experiments carried out with free CAN (CAN/substrate = 0.1). Table 5 shows that CAN/SiO<sub>2</sub> catalyst gave in a first

use, almost the same conversion as free CAN though the selectivity was slightly better. Furthermore, the CAN/SiO<sub>2</sub> reagent separated by filtration at the end of a reaction and washed several times by methanol in order to remove most of DKM absorbed onto silica, still exhibited a notable catalytic activity. Namely, a 54% conversion was obtained (Table 5, entry 3) under these conditions. These results show that the CAN/SiO<sub>2</sub> catalyst can be efficiently retained and confirm that CAN behaves in the reaction as a catalyst. The loss of activity observed during the second use can be attributed to a leaching of CAN during the reaction and in the course of the different washings of the CAN/SiO<sub>2</sub> cake by methanol. Indeed, a blank experiment carried out with the filtrate obtained after filtering the CAN/SiO<sub>2</sub> suspension in AcOH–CH<sub>3</sub>CN medium at 70°C, led after addition of diethyl malonate to 18% conversion of this substrate into DKM after 5 h (Table 5, entry 4).

Table 5

Oxidation of diethyl malonate into diethyl ketomalonate catalysed by CAN/SiO<sub>2</sub> <sup>a</sup>

No.	Catalyst system	Temp. (°C)	Conv. (%)	Selectivity (%)	Yield (%)
1	'free' CAN	70	84	94	79
2	CAN/SiO <sub>2</sub> (first use)	70	80	100	80
3	CAN/SiO <sub>2</sub> (second use)	70	54	100	54
4	filtrate CAN/SiO <sub>2</sub> <sup>b</sup>	70	18	98	17

<sup>a</sup> Conditions: diethyl malonate = 32 mmol; CAN = 3.12 mmol; silica = 7.5 g, acetic acid = 10 ml; acetonitrile = 10 ml; O<sub>2</sub> = 5 l/h; t = 5 h.<sup>b</sup> Filtrate obtained from CAN = 3.12 mmol, SiO<sub>2</sub> = 7.5 g, acetic acid = 10 ml, CH<sub>3</sub>CN = 10 ml; diethyl malonate added = 32 mmol.

### 3.4. Oxidation of related substrates catalysed by CAN

In order to determine the scope of the efficient utilisation of CAN as an oxidation catalyst of compounds having an activated methylene group, we have investigated the reactivity of related substrates such as other malonate esters and acetylacetone under the same conditions as those used for diethyl malonate.

As expected dimethyl malonate was oxidized with a catalytic activity similar to that observed with DEM although the conversion stops at 70% vs. 86% with DEM.

On the other hand, with acetylacetone, an almost total consumption of the substrate occurred after only 1 h reaction time but a very low yield of oxidation product: (2, 3, 4-trioxo-pentane) was obtained.

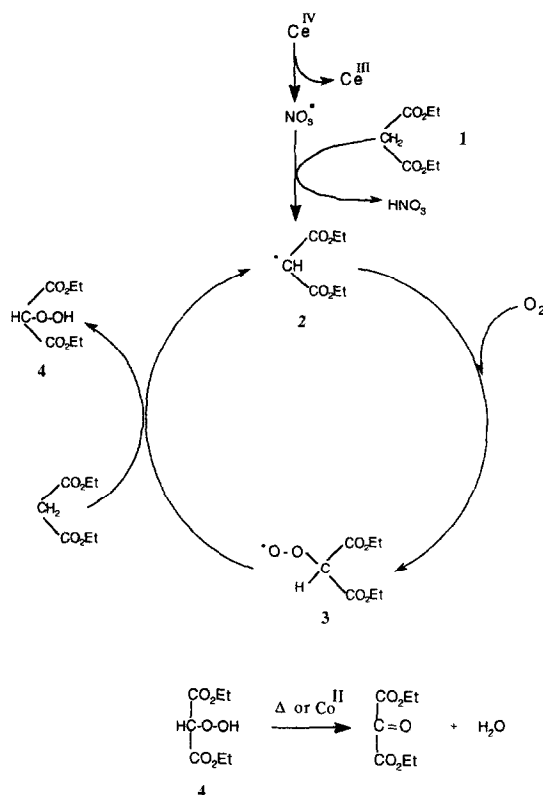
### 3.5. Mechanistic aspect

Although it is difficult to delineate a detailed catalytic cycle precisely, upon analysis of above experiments and from the literature data some conclusions can be drawn.

It is well known that electrophilic carbon radical like  $\dot{\text{C}}\text{HX}_2$  or  $\dot{\text{C}}\text{HXY}$  (with X and Y electron withdrawing groups, i.e. COR,  $\text{NO}_2$ ,  $\text{CO}_2$ ,  $\text{CO}_2\text{R}\dots$ ) can be generated by reactions of  $\text{CH}_2\text{X}_2$  or  $\text{CH}_2\text{XY}$  species with metal ions like  $\text{Ce}^{4+}$ ,  $\text{Co}^{3+}$  or  $\text{Mn}^{3+}$  which are one electron oxidants (the formation of these radicals is unambiguously evidenced by the reaction of these species with alkenes or aromatics to give addition or substitution products [19,26]).



In our case, in the absence of alkenes or arenes, the malonyl radical **2** formed by action of CAN or  $\text{M}^{n+}$  ( $\text{M} = \text{Mn}^{3+}$  or  $\text{Co}^{3+}$ ) on DEM can also be intercepted by molecular oxygen to lead to a peroxy radical **3** which can react with another malonate molecule giving a hydroperoxyde **4** and regenerate the initial malonyl radical **2** (see Scheme 1).



Scheme 1.

Finally this last species **4** decomposes into diethyl ketomalonate and  $\text{H}_2\text{O}$ . This last step occurs either simply at high temperature or with the catalytic assistance of  $\text{Co}^{2+}$  ions at low temperature ( $< 50^\circ\text{C}$ ) (vide supra).

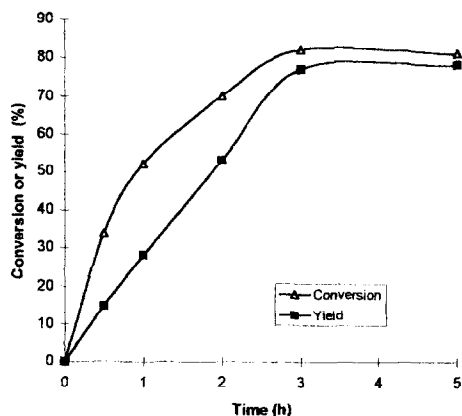
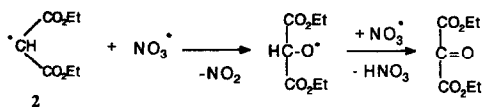


Fig. 1. Oxidation of diethyl malonate catalysed by CAN: conversion and yield vs. time.



Scheme 2.

This assumption is in agreement with the fact that in the first stage of the reaction, the mass balance indicates an important difference between diethyl malonate consumption vs. diethyl ketomalonnate formation (see Fig. 1) although at the end of the reaction this difference disappears. From this remark, this lack of reaction product is not ascribable to a degradation of the substrate and/or product, and therefore probably results from the formation of an intermediate undetected by chromatographic analyses such as hydroperoxyde.

In this process CAN acts as a generator of free radicals allowing the initiation of the chain process which can proceed further without new consumption of CAN.

However as in the absence of oxygen an appreciable part of DEM was transformed into DKM (see Table 3, entry 9), we can assume that under these conditions oxygen was supplied by CAN probably via  $\text{NO}_3^\cdot$  radicals according to the reactions outlined in Scheme 2. In the same way, in the presence of oxygen, it is also possible that part of DEM reacts according to this latter mechanism. The fact that two  $\text{NO}_3^\cdot$  radicals and one malonyl radical are consumed in this process, may explain that the reaction stops before total conversion, as usual in chain reactions.

#### 4. Conclusion

Direct oxidation of malonate esters into ketomalonnates by oxygen or air is efficiently achieved in the presence of cerium ammonium nitrate in catalytic amount. The use of CAN instead of the Co/Mn system previously re-

ported leads to a better yield in ketoester particularly at high conversion. Moreover, CAN is active in the presence of air as source of oxygen in contrast with Co/Mn that requires pure oxygen.

#### References

- [1] O. Achmatowicz Jr., J. Jurczak, J.S. Pyrek, *Tetrahedron* 32 (1976) 2113.
- [2] R. Bonjouklian, A. Ruden, *J. Org. Chem.* 42 (1977) 4095.
- [3] O. Achmatowicz Jr., A. Zamojski, *Rocz. Chem.* 42 (1968) 453.
- [4] J.L. Riebsomer, D. Stauffer, F. Glick, F. Lambert, *J. Am. Chem. Soc.* 64 (1942) 2080.
- [5] A.G. Schultz, Y.K. Yee, *J. Org. Chem.* 41 (1976) 56.
- [6] M.F. Salomon, S.N. Pardo, R.G. Salomon, *J. Am. Chem. Soc.* 102 (1980) 2473.
- [7] M.F. Salomon, S.N. Pardo, R.G. Salomon, *J. Org. Chem.* 49 (1984) 2446.
- [8] O. Achmatowicz Jr., J. Szymoniak, *J. Org. Chem.* 45 (1980) 1128.
- [9] *Organic Syntheses, Col.*, 2nd ed., vol 1, Wiley, New York, p. 266.
- [10] J. Faust, R. Mayer, *Synthesis* (1971) 411.
- [11] S.N. Pardo, R.G. Salomon, *J. Org. Chem.* 46 (1981) 2598.
- [12] R. Sauti, G. Cometti, A. Pagani, EP 85 107495 (1985) to Montedison S.p.A.-CA 104: 224573t.
- [13] W.S. Trahanovsky, P.J. Flash, L.M. Smith, *J. Am. Chem. Soc.* 91 (1969) 5068.
- [14] P. Soucy, T.L. Ho, P. Deslongchamps, *Can. J. Chem.* 50 (1972) 2047.
- [15] H. Tomioka, K. Oshima, H. Nozaki, *Tetrahedron Lett.* 23 (1982) 539.
- [16] L. Syper, *Tetrahedron Lett.* 37 (1966) 4493.
- [17] S. Torii, H. Tanaka, T. Inokuchi, S. Nakane, M. Akada, N. Saito, T. Sirakawa, *J. Org. Chem.* 47 (1982) 1647.
- [18] S. Maimi, L. Mandolini, C. Rol, *J. Org. Chem.* 43 (1978) 3236.
- [19] E. Bacisuchi, D. Dell'Aira, R. Ruzziconi, *Tetrahedron Lett.* 27 (1986) 2763.
- [20] A.J. Colussi, E. Ghibaudi, Z. Yoan, R.M. Noyer, *J. Am. Chem. Soc.* 112 (1990) 8660.
- [21] K. Sakota, Y. Kamiya, N. Ohto, *Can. J. Chem.* 47 (1969) 387.
- [22] J.M. Anderson, J.K. Kochi, *J. Am. Chem. Soc.* 92 (1970) 2450.
- [23] W.S. Trahanovsky, L. Brewster Young, G. Brown, *J. Org. Chem.* 32 (1967) 3865.
- [24] J.M. Brégeault, *Catalyse homogène par les complexes des métaux de transitions*, Masson ed., Paris, 1992, p. 204.
- [25] A. Fischer, G.N. Henderson, *Synthesis* (1985) 641.